A STUDY OF

THE OXIDATIVE DETERIORATION OF MINERAL LUBRICATING OILS

A thesis presented to the University of Glasgow in accordance with the regulations governing the award of the Degree of Doctor of Philosophy in the Faculty of Science

by

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SUMMARY

SUMMARY

The effect of oil composition on its behaviour under oxidative conditions, both by air-blowing and in an internal combustion engine, was the main purpose behind this research programme. Initially it was necessary to devise techniques for the accurate determination of molecular weight and chloroform insolubles, and to modify various other methods of analysis so that they were suitable for this particular work.

An ebullioscopic technique involving the use of a thermistor sensing element was used to determine molecular weight, but rather severe fluctuations were experienced in the meter readings. In an attempt to rectify this the cold finger condenser was replaced by a permanently fixed Liebig condenser - thus giving a constant volume of solvent in the ebulliometer. However, this was not the complete answer to the fluctuations, these being finally eliminated by the use of benzene (as solvent) which had been carefully re-distilled and dried over sodium wire. Apparently moisture was the principal factor causing the inaccuracies.

Segregation of that part of the oil insoluble sludge derived from engine wear and blow-by particles was carried out by taking up the engine deteriorated oil in chloroform and filtering off the extraneous material. This was made possible by the ease with which the oil and the sludge produced by oxidation of the oil could be dissolved in this particular solvent. The minimum amount of chloroform required per gramme of deteriorated oil was established, as was the most efficient method of solvent removal, i.e. rotary film evaporation. This treatment of the used oil sample did not effect the structure or composition of either the oxidised or unoxidised portions.

In this programme several oils of different compositions were oxidised by air-blowing at 200°C (a modified I.P. oxidation test), and by running under

steady conditions in an internal combustion engine for various periods of time. In general, the pattern of deterioration by oxidation was similar in both systems, i.e. the oxidative deterioration followed the path of:

hydrocarbons → resins → oil soluble sludge → oil insoluble sludge

The oils used in this programme all behaved in a similar fashion under these conditions, but differed from one another in the amounts of various oxidation products produced.

The extent to which any one oil followed the path of oxidation outlined above was apparently governed by the percentage of aromatic material contained in the original oil. Some evidence was obtained supporting the theory of "optimum aromaticity" in the range of 6-8% aromatics. This effect was very evident in oils oxidised by air-blowing but was less obvious when the same oils were deteriorated in the engine.

In this work it was shown that a similar optimum effect existed when the ratio of aromatics : naphthenics was considered. At aromatic concentrations lower than 7 or 8% insufficient oxidation inhibiting materials, e.g. naphthols, were formed to prevent the formation of oil soluble sludge, and at this "optimum aromaticity" enough inhibitor was formed to limit the oxidation to the production of resins. Where the aromatic content was high the amount of inhibitor formed was not even sufficient to prevent the oxidation process to proceed yet another step to oil insoluble sludge.

Conditions in the engine appeared to favour oil soluble sludge formation but not the formation of oil insoluble sludge. It may have been that the metals present counteracted the effect of the inhibitors formed, thus allowing soluble sludge, and that insufficient time had been spent at engine conditions for insoluble sludge to be produced.

In both methods of deterioration the same hydrocarbon types were oxidised to give similar oxidation products. The material which was removed upon oxidation and treatment with fuller's earth was found to be spread over the hydrocarbon types present in the original oil with a tendency for the heavier aromatic material to be preferentially attacked. This tendency was more apparent in the oils containing most aromatics.

The tendency for hydrocarbons to be oxidised to resins, then to oil soluble sludge, and finally to oil insoluble sludge was made more apparent by the evidence found during this programme of work. A transfer of material apparently took place from resins, via soluble sludge, to insoluble sludge. In addition, it was found that the acidity of the oil insoluble sludge was related to its insolubility in the oil - this may have been due to the formation of hydroxy acids (by the oxidation of oil soluble sludge) which are known to be insoluble in mineral lubricating oils.

CHAPTER I

CHAPTER I.

Introduction

Lubricating oils derived from petroleum products are the most common lubricants in use at the present time. These oils have to withstand severe conditions of temperature and pressure, as well as acting as heat transfer agents, as carriers for oxidation and corrosion inhibitors, and as anti-friction agents. They have many different specifications to meet dependant on the conditions under which they are used, but by far the most important factor is that they should suffer as little deterioration as possible when in service.

Although there have been many advances in refining techniques and in the development of additives, the life of a lubricating oil is still limited. In the course of the lifetime of an oil it may become contaminated by extraneous material such as dust, water, metal fragments from wear of the engine surfaces, and lead salts from incompletely burnt fuel, all of which make the lubricant less efficient. However, this is of less importance than the changes in the characteristics of the oil which result from oxidative attack on the oil molecules themselves.

Unfortunately, the conditions in an internal combustion engine are precisely those which promote the oxidative deterioration of lubricating oils, viz. splashing of hot oil on metal surfaces with the resulting contact of thin oil films with hot air. Deterioration of this kind results in viscosity increase, acid and sludge formation, and may be the cause of bearing corrosion, lacquer formation, piston ring sticking, etc, in an engine. As engine design

advances, higher cylinder and crankcase temperatures have to be dealt with, and hence lubricating oils have to withstand even more stringent conditions.

A great deal of information, concerning the mechanism of oil oxidation can be gleaned by employing simple systems in which the variables are few and under control. Although the variables present in an internal combustion engine are much more complex, it is still necessary to investigate the deterioration of oils in an internal combustion engine since this is the type of environment in which they are used. The following work is, therefore, an attempt to throw some light on the influence of the chemical structure of the oil on its oxidative deterioration in an internal combustion engine as well as in simple laboratory systems.

CHAPTER II

CHAPTER II.

Nature of Mineral Lubricating Oils

Crude petroleum is, apart from a few impurities, an intricate mixture of hydrocarbons which vary in molecular size from simple compounds like methane to compounds of very high molecular weight and low volatility. The hydrocarbons present in a lubricating oil range from normal alkanes to condensed ring aromatic-naphthenic compounds with alkyl side-chains. The source of the crude oil and its refining treatment are the factors determining the amounts of each hydrocarbon type present in the final product.

Owing to the complex nature and high molecular weights of the hydrocarbons occurring in lubricating oils, separation into pure compounds is virtually impossible. Frantional distillation of lubricating oils (1,2), and analysis of the narrow fractions produced, have in some cases shown that all the fractions have similar distributions of aromatic and naphthenic hydrocarbons.

On the other hand, when a particular Mid-Continent oil was fractionated by reflux solvent/solvent extraction (3) it was found that the first extracts contained polycyclic aromatics with short side-chains; the middle ones contained a little naphthenic material with medium length side-chains; the end fractions consisted solely of naphthenes with very long side-chaines.

It cannot be assumed that the hydrocarbons present in lubricating oils consist of mixtures of separate aromatics and naphthenes since these could easily be distinguished by the usual physical processes of separation. Rather it is thought that the aromatic rings are bombined with the naphthenic rings

in varying ratios as shown by Rossini (4) and others (5,6) by solvent extraction of a Ponca City crude.

It is known that the only pure hydrocarbons which can be considered as separate constituents of lubricating oils are highly branched paraffins, and much work has been done to determine whether or not iso-paraffins are present in lubricating oils. For example, Waterman and Van Westen (7), Muller and Neyman - Pilat (8) and Mair and Willingham (6) all investigated wax-free fractions from various crudes and found that they contained no appreciable amounts of iso-paraffins. However, mass spectrographic studies have in fact shown the presence of iso-paraffins and therefore one should not exclude them. It is now generally accepted that lubricating oils contain either no iso-paraffins or only a minute quantity of them.

Unsaturated compounds have yet to be detected in straight run gasolines and gas oils, and it is not likely that they will be present in lubricating oil fractions. The addition iodine numbers of lubricating oils are usually very small unless distillation has produced some decomposition, e.g. Sachanen and Virobianz (9) showed that the bromine numbers of lubricating oils produced in high vacuum from various crudes ranged from 0.2. to 5.0. High boiling fractions of asphaltic crude oils, which are appreciably decomposed above 350°C., usually give the highest addition numbers.

Fred and Putscher (10) proved recently that Pennsylvanian crudes contained a considerable amount of olefins, these findings being substantiated by Haak and Van Nes (11). Opinion has it, however, that Pennsylvanian crude oil is exceptional, and that there are little or no olefins present in crude oils or in straight run distillates.

From the foregoing evidence, and other evidence in the same vein, it has been concluded that lubricating oils consist of :

A. Paraffins, or saturated hydrocarbons with straight or branched chains;

B. Naphthenes, or saturated cyclic hydrocarbons of one or more rings which may have paraffinic side-chains;

C. Aromatics, or hydrocarbons containing one or more aromatic nuclei which may have naphthenic rings and/or paraffinic side-chains.

The properties of any particular oil will be dependant on the ratio of the above hydrocarbon types present, and also on the manner in which they are combined.

Molecular Structure of Lubricating Oils.

In order to gain some insight into the nature of the aromatics present in lubricating oils, various types of pure aromatic hydrocarbons have been added to oils which have been de-aromatised (12) and the properties of these new oils compared with the original ones. Work of this type has led to the conclusion that the aromatic hydrocarbons present in lubricating oils should resemble polycyclic aromatics with comparatively short side-chains, or monocyclic aromatics with naphthenic rings on their side-chains.

The naphthenic material left in de-aromatised lubricating oils of varying origin has been extensively examined (13,14,15) and its empirical formula given as $C_n H_{2n-2}$ to $C_n H_{2n-8}$ and the formulae for the aromatic hydrocarbons removed varied from $C_n H_{2n-6}$ to $C_n H_{2n-44}$. This would seem to indicate

that the hydrocarbons in any lubricating oil contain from two to five condensed rings.

The question of the number of carbon atoms per ring was discussed by Lipkin and Kurtz (16,17), and they reached the conclusion that more than half of the rings in lubricating oil hydrocarbons are five-membered - the corrected average figure being given as 5.7. The actual number of five and six-membered rings in the molecule may be in some doubt, but it can be assumed that five and six-membered rings are normally present. Verification of this can be found in Grosse's work (18) using optical exaltation in which he demonstrated the absence of C_3, C_4, C_7 and C_8 rings in lubricating oil hydrocarbons.

Paraffinic side-chain length appears to be dependant on the type of ring to which it is attached. The number of carbon atoms in a paraffin side-chain varies from 5 to 20, long chains being associated with naphthenes and short chains with aromatics. At first it would seem unlikely that long side-chains of C_{12} and over would remain in lubricating oils after de-waxing, since it is known that derivatives of benzene, naphthalene, etc, with long side-chains all having melting points above 10°C. However, branching in the side-chain lowers the melting point considerably (19,20) and this may provide the means by which long chains can exist in lubricating oil hydrocarbons.

A commonly used technique in the study of lubricating oils has been the comparison of the properties of synthetic hydrocarbons with those of oils. These synthetic lubricants have been prepared by the alkylation of polycyclic aromatics, and upon examination (21,22) were found to have lubricating properties provided that they possessed one or more sufficiently long paraffinic

side-chains and was independant of the structure of the remainder of the molecule. Synthetic lubricating hydrocarbons have been investigated thoroughly by Mikeska (19,23) who found that the lubricating properties depend on the number of rings, ratio of aromatic to naphthenic rings, ratio of rings to paraffins and the number, length, degree of branching, and position of the side-chains.

Summing up, it would be unwise to assume that lubricating oils consist only of polycyclic hydrocarbons made up of a condensed nucleus to which is attached one long branched drain and several short chains. The concept (24) of a simple "model molecule" for all lubricant hydrocarbons has only found support from other sources in respect of the single nucleus theory (25), but the idea of only one long side-chain attached to the nucleus in aromatic lubricants has been disputed (26). Alkylbenzenes of the structure proposed by Hood et al are not the sole explanation for the mass spectrum given by a lube oil concentrate. Some di-n-alkylbenzenes and secondary, tertiary and side-chain-branched mono-alkylbenzenes give similar results. Another indication that the picture of a simple model for the entire petroleum distillate range is not entirely true, comes from the work of Martin, Winters and Williams (27) who examined the C_{10} alkylbenzenes of crude oil components and discovered wide variation in isomer distribution in different crudes.

Structural Group Analysis

In the characterisation of the structure of lubricating oils a hypothetical mean molecule is considered and the distribution of carbon atoms among paraffinic, naphthenic and aromatic structures determined together with the number of aromatic and naphthenic rings in this mean molecule. This is

known as "structural group analysis" and the average proportion of the several structural groups are estimated irrespective of the manner in which the groups are combined in the molecule.

The "direct" method of structural group analysis is based on a theoretical study of hydrocarbon molecules in which ultimate analysis and molecular weight determinations are carried out before and after hydrogenation. A paraffin molecule of a given molecular weight will have a definite and deducible percentage of hydrogen. With the introduction of naphthenic rings into this molecule each one added results in the loss of two hydrogen atoms. Any saturated molecule containing naphthene rings will, therefore, have a lower hydrogen content than the paraffin of the same molecular weight, and hence it should be possible to establish a direct relationship between hydrogen content, molecular weight and the number of rings per molecule in a saturated hydrocarbon (28). This relationship is as follows:

$$R_N = 1 + (8.326 - 0.5793H)M/100$$

where R_N is number of naphthenic rings per molecule

H is percentage of hydrogen

M is the molecular weight

When a molecule containing aromatic rings is hydrogenated to saturated rings, each aromatic carbon atom adds a hydrogen atom. The hydrogen taken up in the hydrogenation of double bonds is thus a measure of the number of aromatic rings present. The resulting saturated molecule can be analysed as before, except that the percentage hydrogen is now a measure of the total rings present in the original molecule. Naphthenic rings can be obtained from total rings and aromatic rings by difference, and in this manner a picture of the hypothetical

mean molecule can be built up and thus the carbon distribution calculated.

Certain assumptions require to be made regarding the number of carbon atoms per ring and to what extent ring condensation and ring linkage occur before a complete structural group analysis may be derived. Kata-condensed, six-membered rings have been the final choice as the basis for calculation and the reasons for this are given in some detail by Van Nes and Van Westen (28).

The "Waterman Ring Analysis" was the first published method for structural group analysis (26), and it is based on the additivity properties of hydrocarbons. For increments of carbon and hydrogen, it was noted that the Lorentz - Lorenz specific refraction

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

(Where n is refractive index at 20°C using the sodium D line, and d is density at 20°C.)

was additive. Hence "r" is proportional to the percentage hydrogen in hydrocarbon molecules and therefore the measurement of specific refraction and molecular weight in a saturated oil sample leads to the calculation of the number of rings per molecule. The Waterman Ring Analysis has proved to be much more suitable for routine analysis than the "direct" method.

The same authors (29) also gave a method of analysing samples containing aromatic rings involving the measurement of the aniline point. The value was then compared with the aniline point for the completely hydro-genated sample of the same molecular weight and specific refractivity, as the

original sample, the second aniline point being obtained graphically. The difference in the two aniline points was then, by means of suitable factors, employed to give the percentage of aromatic rings and to predict the specific refraction of the sample if it were completly hydrogenated.

In order to eliminate the measurement of aniline point, a "density method" (28) was introduced in which aromatic content and specific refraction of a completely hydrogenated fraction were determined from density measurements. Analysis had now been reduced to the measurement of refractive index, molecular weight and density. During attempts to simplify the density method equations for obtaining carbon distribution and ring content were evolved in terms of these three quantities which eliminated the need to calculate specific refraction. These equations are the basis of the "n-d-M method" of structural group analysis.

Of the three determinations required for analysis the estimation of molecular weight presents the greatest difficulties and a more recent publication (30) gives a method which replaces the measurement of molecular weight by the measurement of kinematic viscosity. This is known as the "V_k-n-dmethod".

n-d-M Method of Structural Group Analysis

This method is based on the statistical analysis of a large number of mineral oil samples from different sources (25) and involves the determination of the physical constants refractive index (n) density (d) and molecular weight (M).

The percentage carbon in total ring structure (% C_R) and aromatic ring structure (% C_A), the mean total number of rings per molecule (R_T) and

aromatic rings per molecule (R_A) may be calculated from general equations of the type.

$$C = \frac{a}{M} + b \cdot d + c \cdot n$$

$$\text{and } R = a' + b'M \cdot d + c'M \cdot n$$

where C = percentage carbon in one type of structure

R = mean number of rings per molecule

d = the difference between measured density (d) and the density of the limiting paraffin (a liquid hypothetical paraffin containing an infinite number of CH_2 groups) at the same temperature

n = A similar function for refractive index

M = Molecular weight

and a, b, c, a', b', and c' are constants

The originators of the formulae, Van Nes and Van Westen, found that two equations were necessary for each quantity to be calculated since one equation did not cover the range accurately enough. This was thought to be due to the fact that the mean number of carbon atoms per ring decreases as the number of rings increase. Therefore there are equations for "low range" and "high range" aromatic contents.

Percentage carbon in paraffinic structure (% C_P) in naphthenic structure (% C_N) and the mean number of naphthenic rings per molecule (R_N) are estimated by difference.

This method is primarily intended for the structural group analysis of olefin free petroleum distillates boiling above the gasoline range. Hence it is suitable for lubricating oil fraction since it is based on samples with molecular weight greater than 194. The method is also suitable for fractions containing at least 75% carbon in the ring structure, where the aromatic rings

do not exceed the naphthenic rings by more than one-and-a-half times, and fractions having up to four rings per molecule with not more than half of them aromatic. It can also be used for oils up to 0.2% sulphur and up to 0.5% nitrogen and oxygen.

The equations used in the determination of the n-d-M analysis are as follows (where S is sulphur content):

$$d' = d - 0.8510$$

$$n' = n - 1.4750$$

Two factors, v and w are determined and used in the calculations.

$$v = 2.51\ n' - d'$$

$$w = d' - 1.11\ n'$$

The percentage carbon in aromatic structure is given by:

for v positive $\%C_A = 430\ v + \frac{3660}{M}$

for v negative $\%C_A = 670\ v + \frac{3660}{M}$

The percentage carbon in ring structure is given by:

for w positive $\%C_R = 820\ w + \frac{10,000}{M} - 3S$

for w negative $\%C_R = 1440\ w + 10,000 - 3S$

The percentage carbon in naphthenic and paraffinic structures is given by:

$$\%C_N = \%C_R - \%C_A$$

$$\%C_P = 100 - \%C_R$$

The mean number of aromatic rings per molecule is given by:

for v positive $R_A = 0.44 + 0.55\ Mv$

for v negative $R_A = 0.44 + 0.080\ Mv$

The mean total number of rings per molecule is given by:

for w positive $R_T = 1.33 + 0.46\ M\ (w - 0.005S)$

for w negative $R_T = 1.33 + 0.180\ M\ (w - 0.005S)$

The mean number of naphthenic rings per molecule is given by:

$$R_N = R_T - R_A$$

A similar series of equations is available for measurements of refractive index and density at 70°C. when these are not available at 20°C. Nomographs for rapid determination of equations are also available but of course are not quite so accurate (28).

CHAPTER III

CHAPTER III

Hydrocarbon Oxidation

Low temperature, liquid phase oxidation of hydrocarbons has been the subject of much investigation (31,32,33,34,35,36) the main interest being in the mechanism of oxidation from the point of view of deterioration of lubricating oils.

In earlier studies of hydrocarbon oxidation the greatest difficulty was found to be the isolation of primary oxidation products. At first it was thought (37) that alcohols were intermediate oxidation products, and that other products then came from the oxidation of the alcohol. This theory was proposed by Bone for high temperature oxidation in the gaseous phase but later Stevens (38) doubted whether it was valid for liquid phase oxidation at lower temperatures. More recent work (39) has upheld Stevens' view by demonstrating that alcohols are generally less easily oxidised than the corresponding hydrocarbon, and in some cases act as inhibitors to oxidation. Bach (40) and Engler and Wild (41) were first to propose the modern theory based on the assumption that a hydroperoxide is the primary reaction product of hydrocarbon oxidation. This mechanism was further developed by Callender (42) and Ubbelohde (43) and extended to hydrocarbons as a whole by Farmer (44) Chavanne (45) and Stevens (46).

Oxidation of high molecular weight paraffins and alkyl benzenes at 100°C. to 120°C. (47) gave hydroperoxides as main oxidation products, and in the case of paraffins these hydroperoxides decomposed to give ketones in high yield. In the case of hydrocarbons oxidised at 30°C to 100°C. (48) in the oxidation of decalin at 110°C. (49), and in the oxidation of white oils (50,51)

hydroperoxides were found to be present in high concentration in the early stages of the reaction.

In the oxidation of n-decane, n-nonane, and n-octane, at 120°C. (52,53,54) the main products were found to be methyl octyl -, methyl heptyl - and methyl hexyl ketones with carboxyllic acids ranging from formic acid to acids containing one less carbon atom than the original hydrocarbons. This suggested that a beta-carbon atom was attacked primarily and agreed with the theory (55) that in low temperature oxidation the beta-carbon is primarily involved, followed by gamma-carbon and so on towards the centre of the hydrocarbon molecule.

(a) Oxidation of Paraffins:

Employing the evidence outlined above, Zuidema (56) suggested that the mechanism of low temperature, liquid phase oxidation of straight chain paraffins may be as follows:

$$R.CH_2.CH_2.CH_3 + O_2 \longrightarrow \underset{\text{Hydroperoxide}}{R.CH_2.\overset{O.OH}{\overset{|}{C}}H.CH_3} \longrightarrow \underset{\text{Ketone}}{R.CH_2.CO.CH_3} + H_2O$$

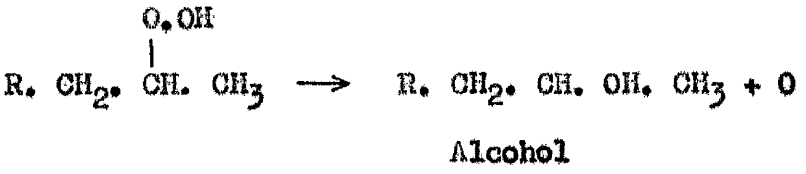
$$R.CH_2.CH_2.CH_3 + O_2 \longrightarrow \underset{\text{Acid}}{R.CH_2.COOH} + \underset{\text{Formaldehyde}}{H.CHO}$$

$$R.CH_2.COOH + O_2 \longrightarrow \overset{O.OH}{\overset{|}{R.CH}}.COOH \longrightarrow \underset{\text{Aldehyde}}{R.CHO} + CO_2 + H_2O$$

There should be some attack on the gamma-carbon atom also, to give the ethyl ketone, with the resultant production of a carboxyllic acid smaller

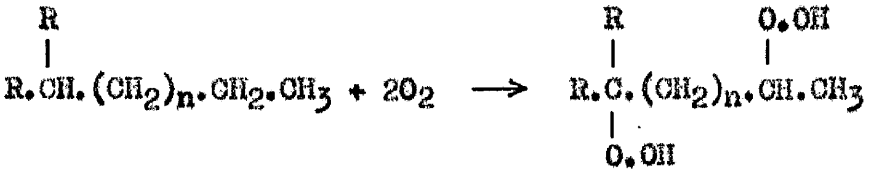
by one carbon atom, and acetaldehyde. Complete breakdown of the paraffin chain may come about by the alternate formation of acid and carbonyl.

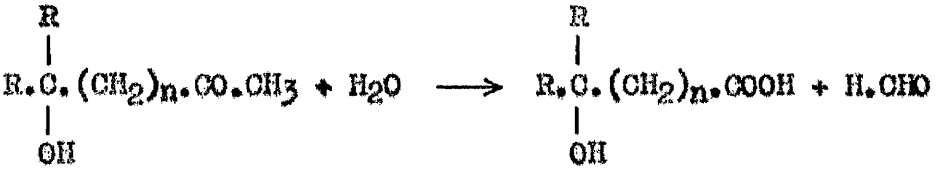
Formation of alcohols requires the hydroperoxide to be reduced, losing an atom of oxygen in the process:



Alcohol

When a branched chain paraffin is oxidised there are two points of attack, a tertiary and a secondary hydrogen atom, and may proceed either simultaneously or in stages depending on the reaction conditions.





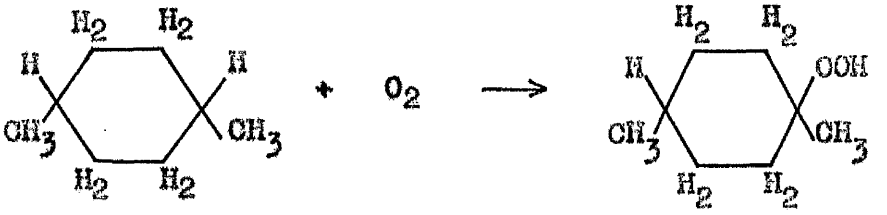
Hydroxy Acid

(b) <u>Oxidation of Naphthenes:</u>

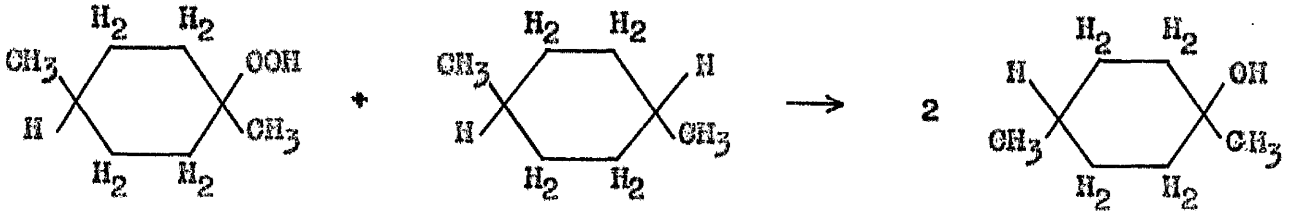
Chavanne and co-workers (52,53) made an extensive study of the oxidation of 1:4-dimethyl-cyclohexane and a few cyclo-pentane derivatives. In the case of 1:4-dimethyl-cyclohexane the principal product was dimethyl-cyclohexanol, with water, carbon dioxide, β-methyl-δ-acetylvaleric acid, acetic acid, β-methylvaleric acid, dimethyl-cyclohexanediol and acetonyl-lactone also being formed. Small amounts of hydrogen, carbon monoxide,

methane, ethane and formic acid were produced.

As in the case of paraffins a hydroperoxide is formed and it is thought, from the evidence cited above, that attack takes place at a tertiary carbon atom.



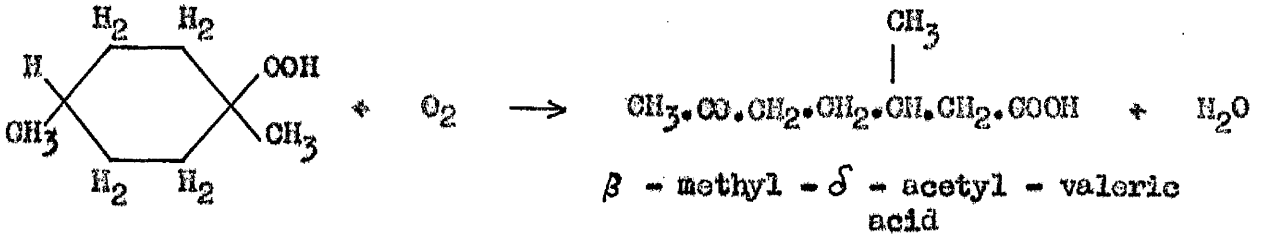
1:4 dimethylcyclohexane hydroperoxide



1:4 dimethylcyclohexanol

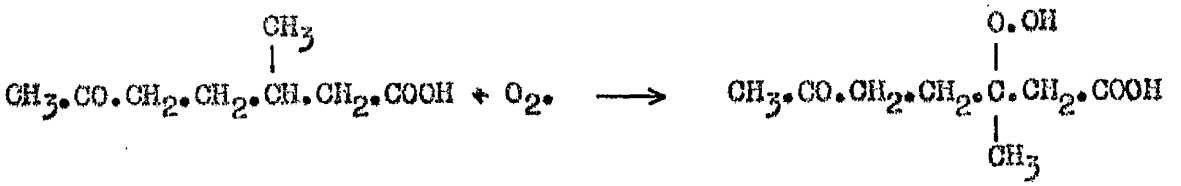
Formation of the diol may be explained by a similar mechanism.

Other products are formed by the oxidation of the hydroperoxide itself and not the ketone as with the oxidation of paraffins. Instead of reduction of the hydroperoxide to form an alcohol, further oxidation of the naphthenic ring gives a product with the same number of carbon atoms as the original hydrocarbon.

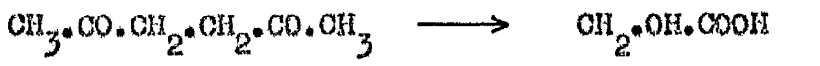


β - methyl - δ - acetyl - valeric acid

If the other tertiary carbon atom in this molecule is attacked then acetonyl acetone will be formed.



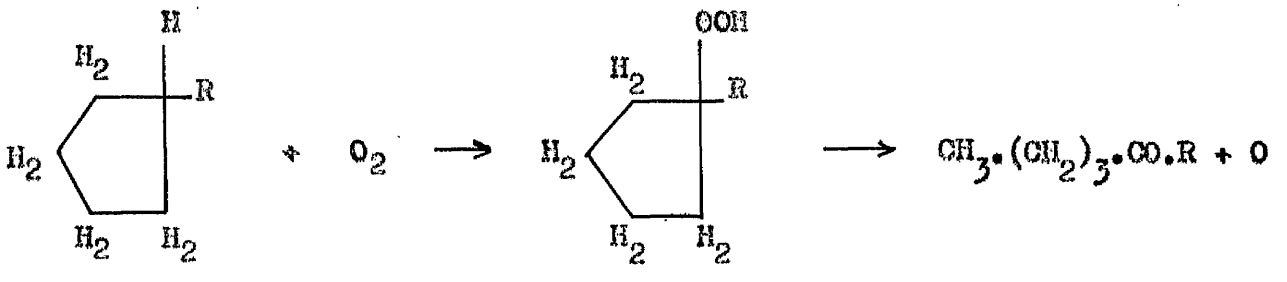
hydroperoxide



acetonyl acetone glycoloc acid

Some of these oxidation products are probably oxidised further to more simple products and methane, ethane, etc, are probably formed by cracking.

Oxidation of ethyl-, butyl-, and phenyl-cyclopentane (54.) indicates that here the mechanism is different from that for six-membered rings. Whereas cyclohexane derivatives gave a ketone with one carbon atom less, the above cyclopentanes produced ketones containing the same number of carbon atoms as the original hydrocarbon. This may have been due to reduction of the hydroperoxide, formed at the tertiary carbon atom, to an aliphatic ketone rather than to a cyclic alcohol as in case of cyclohexane derivatives.



Further oxidation of the hydroperoxide can also take place to give keto derivatives of aliphatic acids.

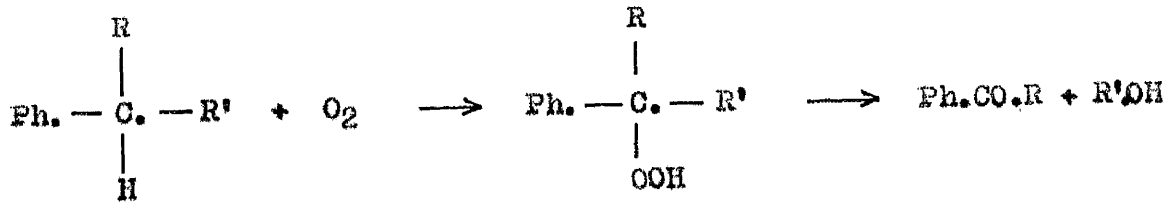
There is still some uncertainty as to why there is a difference between cyclohexane and cyclopentane derivatives, though it is thought that it may be due to the presence of two tertiary groups in cyclohexane derivatives and only one in cyclopentanes, or to differences in ring size or side chain length.

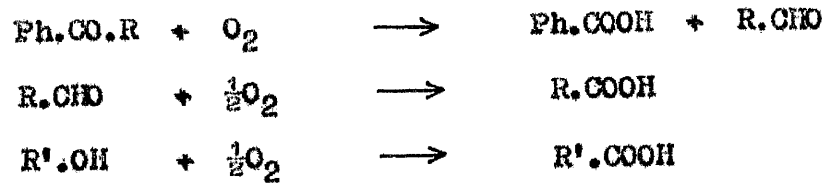
(c) Oxidation of Aromatics:

Oxidation of a series of benzene derivatives at 80°C. to 140°C. showed that the oxygen attack is always at a carbon atom attached to the benzene ring (57,47). Aldehydes containing the same number of carbon atoms as the original hydrocarbons were produced by methyl benzenes, while ketones were produced by substituted benzenes containing one or more alkyl groups larger than methyl. When the carbon atom attached to the benzene was tertiary, the ketone was found to contain the smaller of the two groups attached to the carbon atom, the larger group splitting off to give a low molecular weight acid. This was also found to be true when one of the two groups was a phenyl group

It seems probable that the formation of a hydroperoxide group at the carbon adjacent to the benzenes ring was the initiating step, and subsequent studies (58) have shown that this is undoubtedly so. A peroxide could decompose by dehydration to the aldehyde or ketone, depending on whether the starting material contained methyl or larger groups, or by the loss of a molecule of alcohol to form a ketone in the case of a tertiary hydrocarbon. Acids could be produced from both aldehydes and ketones by oxidation.

The reaction mechanism is well illustrated by the following general case in which R is smaller than R':





No rupture of the benzene ring occurs when aromatic hydrocarbons are oxidised, and dark, insoluble condensation products are always produced.

Oxidation Rates

For pure hydrocarbons four types of oxygen absorption curves can be obtained - autocatalytic, autoretardant, linear, and an autocatalytic: autoretardant type (59). These curves only apply under a given set of oxidation conditions as it has been shown (60) that a given hydrocarbon may exhibit autocatalysis or autoretardation depending on temperature at which the reaction occurs.

Oxidation rates of pure hydrocarbons may be determined arbitrarly by measuring the time required for 2000cc of oxygen to be absorbed by one gramme mole (59?. The greatest rates have been found to be associated with hydrocarbons containing a partially hydrogenated condensed ring or a benzene ring with a long paraffin side-chain, but these did not give an autocatalytic curve, as one might have expected showing that autocatalysis was not required for rapid oxidation. The most stable hydrocarbons was found to be the naphthalene derivatives; most of them gave linear or autoretardant absorption curves.

An increase in stability was noted when long side chain alkyl benzenes were hydrogenated to cyclohexane derivatives, but similarly hydrogenated naphthalene derivatives showed a decrease in stability. This was found to be especially so if the naphthalene ring was only partially hydrogenated. Thus, naphthalene was much more stable than tetrahydronaphthalene which in turn was more stable than decahydronaphthalene. Addition of paraffin side chains to naphthalene, tetralin and decalin greatly reduced the stability of these compounds.

When the primary, secondary and tertiary amyl derivatives of benzene were compared it was found that the tertiary compound was the most stable. This was due to the fact that the tertiary derivative could not form a hydroperoxide at the carbon attached to the ring and hence was oxidised at other positions. The tertiary butyl derivative of benzene was also found (47) to be much more resistant to oxidative attack than the other butyl derivatives.

The extreme stability of naphthalene aromatics, in comparison with the benzene homologs, has been attributed (59) to the differences in their oxidation products in acting as inhibitors. Oxidation of n-amylbenzene after adding 9.8% of pre-oxidised α- methylnaphthalene, gave an oxygen absorption curve which almost coincided with that for α- methylnaphthalene alone.

Saponification values have been used in the study of oxidation stability (61), these values being measured after the hydrocarbons had been oxidised in a bomb under pressure for a fixed period of time. It was concluded that polynuclear aromatics were very stable and that the introduction of side chains reduced the stability, the longer the side chain the greater the decrease. Beta derivatives of naphthalene were found to be more reactive than the alpha derivative. These conclusions of Chernozhukov and Krein (61)

are in close agreement with those of Larsen (59). All of these workers found that benzene derivatives are less stable than naphthalene ones and that higher alkyl compounds are less stable than lower molecular weight ones.

When one comes to deal with mixtures of hydrocarbons the picture becomes much more complicated. The subsequent course of a hydrocarbon oxidation is, to some extent determined by the reaction products. Even with a single hydrocarbon a variety of products can be obtained, so that with mixtures of hydrocarbons the effect of the oxidation products of one hydrocarbon upon the rate and extent of another is almost unpredictable.

A mixture of hexadecane and cis-decalin was apparently oxidised at the same rate as the pure cis-decalin (62) suggesting that the least stable hydrocarbon was preferentially attacked. However, when a mixture of hexadecane and 1 - methylnaphthalene was oxidised, the rate was similar to that of pure 1 - methylnaphthalene and very much slower than that of pure hexadecane. This slow rate of oxidation was associated with the formation of α- naphthol, known to be an oxidation inhibitor.

The above example indicates how unpredictable the oxidation of mixtures can be. A further example of this is to be found in the work done by Larsen et al (59) who found that in blends of white oil containing 25% of diamylnaphthalene, the diamylnaphthalene was oxidised preferentially even though white oil by itself is much more reactive than diamylnaphthalene.

Oxidation of Lubricating Oil Fractions

The oxidation of refined mineral lubricating oils, containing an immense number of different hydrocarbon molecules is a process which defies

at the moment all but a general approach since even in simple mixtures the oxidation products of one component can drastically effect the behaviour of the other. It is generally only possible to analyse for functional groups, and when this wasdone for the oxidation products of a number of Californian oils (50) extracted in stages by furfuraland subsequently oxidised at 150°C., it was observed that as aromatics were removed there was a decrease in sludge formation. This is of course consistent with oxidation studies on pure hydrocarbons which indicate that aromatics give dark insoluble condensation products.

Extraction by furfural also resulted in the production of greater quantities of water and less carbon dioxide and volatile acids. No peroxides were detected, which suggests that any peroxides formed were immediately decomposed into other oxidation products. Both Dornte (50,63,64) and Denison (51) report that when white oil is oxidised at 135°C. the principal products are peroxides, carbonyls, water, acids and only a trace of carbon dioxide. When they oxidised lubricating oil at 175°C. they found that water accounts for 40% and carbon dioxide for 3 - 10% of the oxygen absorbed.

A Pennsylvanian oil oxidised at 170°C. (65,66) gave the oxygen distribution as: water, 44 - 70%; carbon dioxide, 3 - 9%; carbon monoxide, 0.6 - 3.2%; volatile acids, 1 - 7.5% fixed acids, 2 - 2.5%; and 2 - 7% isopentane insolubles (containing 15% oxygen). Temperature apparently exerts little influence on this distribution in range 150-180°C., but it varies as oxidation proceeds. Similar studies at 175°C. (67) found that 34.5 - 43.5% of oxygen absorbed could be accounted for as water and 3.1 - 7.5% and as carbon dioxide.

Hicks-Bruun, et al (67) compared an oil containing 19% aromatic rings with one containing 3% and found that the more aromatic oil produced much greater quantities of "soluble sludge" and "insoluble sludge" than the other. The effect of varying the concentration of aromatics on the time required for absorption of 1800c.c. of oxygen/100gm. oil, in presence of iron, was examined by Van Fuchs and Diamond (58). The curve relating absorption time to aromatic content passed through a maximum at about 5% aromatics, showing that the oil had an apparent "optimum aromaticity" with respect to oxidation stability.

A Pennsylvanian oil containing 9% aromatic was separated (66) into 124 fractions and seven of these fractions, containing 0 - 40% aromatics, were oxidised at 140°C. It was found that none of the fractions was as stable as the original oil, the most stable being those with 15% and 25% aromatics, the least stable those of zero aromaticity.

Oxidation of lubricating oils appears to be concentrated on the aromatic material, and is carried out independant of the oxidation of naphthenes and paraffinics. In low concentrations aromatics retard saturated hydrocarbon oxidation, the oxidation of aromatics themselves being almost negligible. At higher concentrations, however, the oxidation of aromatics is in addition to that of saturated hydrocarbons and may reverse retarding effect of oxidation products.

Kinetics of Hydrocarbon Oxidation

Most liquid-phase hydrocarbon oxidation processes are characterised by the fact that the rate of oxidation increases with the extent of oxidation.

They are said to be autocatalytic, but there is no true catalysis since the hydroperoxide, formed almost quantitatively in the first stages of oxidation (68,44,69,70) is itself used up.

Bolland (71) maintained that the general scheme of liquid-phase hydrocarbon oxidation comprises three steps (1) Initiation, (2) Propagation and (3) Termination.

(i) Initiation

In the initiation a radical is formed (R-$^{\bullet}$)

$$RH \longrightarrow R\text{-} \quad + \quad (H\text{-})$$

where RH is the substance being oxidised. Initiation can be brought about in several ways,

(a) by radiation which splits a molecule into radicals,

(b) by initiators e.g. benzoyl peroxide, which decompose thermally into radicals,

(c) by thermal decomposition into radicals of the hydroperoxide produced in the reaction,

(d) by the reaction of metal catalysts with the hydroperoxide to form radicals, and

(e) by direct reaction between oxygen and the substrate to form an R- radical and an HO_2- radical. This is a very slow reaction and of minor importance.

Of the greatest interest is thermal decomposition of the hydroperoxide since this gives rise to autoxidation (72,73).

Thus:

$$ROOH \longrightarrow RO\text{-} + OH\text{-}$$

$$RO\text{-} + RH \longrightarrow ROH + R\text{-}$$

$$OH\text{-} + RH \longrightarrow H_2O + R\text{-}$$

(ii) Propagation

This takes place in two steps, in the second of which the R- radical is regenerated. The second step is then repeated, forming a chain reaction.

$$R\text{-} + O_2 \longrightarrow RO_2\text{-}$$

$$RO_2\text{-} + RH \longrightarrow ROOH + R\text{-}$$

(iii) Termination

The chains are terminated by the combination of radicals

$$2R\text{-} \longrightarrow R\text{-}R$$

$$R\text{-} + RO_2 \longrightarrow ROOR$$

$$2RO_2\text{-} \longrightarrow ROOR + O_2$$

The rate of reaction depends on the concentration of hydroperoxide. The shape of the autocatalytic oxidation curve can be explained by the fact that the concentration of hydroperoxide is low in the beginning and the reaction accelerates as it builds up. Later on the reaction slows down because of the depletion of material being oxidised.

It is well known that metal catalysis can accelerate these oxidation

processes, by increasing the rate of initiation and the reactions may well be:

$$ROOH + M \longrightarrow RO\cdot + OH^- + M^+$$

$$ROOH + M^+ \longrightarrow RO_2\cdot + H^+ + M$$

These two reactions form a chain whereby the metal ions act as catalysts. The metal ions may act on other reactions in the oxidation but their main effect is to increase the rate of initiation. These metals can be dissolved in the substance being oxidised, but they can also be present in the emulsified aqueous phase of an oxidation. There they react with hydroperoxide that passes into the aqueous phase.

The reaction can be inhibited, i.e. the induction period is increased, by adding small quantities of easily oxidised compounds such as phenols, thiols, amines, etc. These inhibitors usually interfere with the propagation step by giving a hydrogen atom to the radical $RO_2\cdot$. The product formed cannot add oxygen to continue the reaction.

The above scheme of oxidation may be over simplified, but it is thought to be the basis of most liquid-phase oxidations of organic materials by molecular oxygen. The complications appear when we consider the further reaction of radicals and of the hydroperoxide.

CHAPTER IV

CHAPTER IV

Oxidation Tests and Engine Tests

A number of test methods have been devised for the purpose of estimating the probable behaviour of lubricating oils under oxidising conditions. Small scale laboratory tests give useful information but are limited in their scope, whereas engine tests which simulate service conditions are of more practical value.

In laboratory oxidation tests it is usual to bring hot oil into contact with air or oxygen, generally by bubbling the gas through the oil. Many variations of this method have been used but only one has been adopted as standard for lubricating oils in this country. This is the Institute of Petroleum test I.P. 48 (74) originally introduced by the Air Ministry as a test for aviation engine oils. This test has been examined extensively (75) from the point of view of reproducibility of results and the effect of variation in the specified conditions.

In the I.P. 48 test, air at 15 litres/hour is bubbled through oil maintained at 200°C. The stability of the oil is measured by the increase in the Ramsbottom carbon residue and the kinematic viscosity ratio after 12 hours oxidation.

The Indiana oxidation test (76) is similar in principle to the I.P. test, but in this case air at 10 litres/hour is blown through 300ml. of oil maintained at 341°F. Precipitable sludge is taken as the criterion of stability and periods of time are measured for the formation of (a) 10mg. sludge per 10g. oil, and (b) 100mg. sludge per 10g. oil. Viscosities may also be measured.

The Indiana stirring oxidation test for lubricating oils (77) is a modification of the above test and has been developed for oils containing additives. High speed stirring provides aeration of a 250ml. sample of oil maintained at 330°F., in the presence of copper and iron as catalysts. Sludge and acidity are measured every 24 hours, for a maximum of 72 hours, and are taken as measures of the extent of oxidation.

Yet another oxidation test is the Sligh oxidation test (78) which involves a small static oil sample surrounded by an atmosphere of oxygen at 200°C. for a period of 2.5 hours. The asphaltic material produced in this time is taken as a measure of oxidation, and is reported as the "Sligh Number".

Oil stability can also be determined by continuously recording the oxygen absorbed by the oil sample. Dornte (50) first described such an apparatus in which oxygen bubbled through a hot oil sample in a closed circuit. Low molecular weight gases and vapours are removed by an absorption and condensing system and may be measured. The shape of the oxygen absorption versus time curve is often taken as being characteristic of a particular oil sample.

Tests also exist for the measurement of the extent to which an oxidised oil is defective and measure bearing corrosion wear, sludge and lacquer deposition etc. The Existent Corrisivity test (79) is a bearing corrosion test in which no significant oxidation of the oil takes place during the test. A bearing metal specimen is immersed in 200g. of oil at 156°C. for 20 minutes with air agitation at the rate of 6.3ml/min. On the

other hand the Underwood (80) and Thrust (81) tests are examples of bearing corrosion tests in which the oil is oxidised during the test period.

Controlled engine tests are used in the laboratory to simulate true operating conditions and several measurements may be made to estimate lubricant efficiency. The actual conditions in a running engine are such as to rapidly change the initial qualities of the selected lubricant due to oxidation of the oil itself and contamination by the combustion products of the fuel. While it is possible to make a laboratory assessment of the oxidation resistance of an oil, the complications introduced by the various contaminants are by no means easily simulated by a laboratory test procedure. Experience has shown that the laboratory tests do not adequately measure the desirable properties of oils, especially oils containing additives, and the only satisfactory way in which this can be done is by actual running in engines.

Engine tests can be of two kinds - long term trials in which actual vehicles are used running under normal road operating conditions, or bench tests in which the engine is under close control. The "road test" method is very difficult to control and for its success needs a lengthy period and a large number of vehicles.

Ideally, the conditions under which a test engine is run should be based on those pertaining to normal service. In practice this is difficult to arrange, such conditions vary widely and service data is difficult to acquire. Also, any such test would be of far too long duration and it is usual, therefore, to rely on extreme conditions and assume that if satisfactory performance is obtained in such an accelerated test, the lubricant will behave equally well under normal and, usually, less arduous conditions.

The evaluation of the oil is made by observation, quantitative and qualitative, of its effect on the engine. The main characteristics which indicate the probable performance of the oil in service are: ring sticking, piston ring and cylinder wear, bearing corrosion, sludge, deposits in the combustion chamber, and deterioration of the oil itself.

In general it is the state of the engine rather than the condition of the used oil which receives most attention and is regarded as the most important criterion. Provided that satisfactory engine performance has been given the analysis of the used lubricant is considered to be rather unimportant.

A great many engine tests have been devised and many of these tests have been standardised by the Co-ordinating Research Council of America (82). Despite the large number available, little information is given in the literature on the correlation of oxidation tests with engine performance. It is accepted that some tests show little correlation with performance. Larsen, Armfield and Whitney (83,84) showed that three oils could be placed in any of six possible orders of merit by variation of the catalyst in an oxidation test. Matthews and co-workers (85), however, have shown that an oxidation test can provide a good indication of how an oil will perform in an engine test, but stress that the catalytic conditions used in the oxidation test should be as close as possible to those existing in the engine.

Purpose of Research

For some years now a study of the deterioration of lubricating oils has been undertaken in this laboratory (86,87,88). This has been mainly concerned with the oxidation of lubricating oils by blowing air through a hot

oil sample and analysis of the resulting oxidised sample. It was felt that the time was ripe to continue this work by studying the deterioration of lubricating oils in an internal combustion engine.

When an oil is oxidised by blowing air through a hot sample the products of oxidation may be divided into three groups depending upon their solubility in the oil. These are "oil insoluble sludge", "oil soluble, but isopentane insoluble sludge" and the remaining oil soluble oxidised material which are known as "resins". When the oil is deteriorated in an I.C. engine we have another class of oil insoluble material which consists of engine wear particles and carbon particles from the combustion chamber. This material is known as "chloroform insolubles" since all other oil oxidation products are soluble in chloroform (89).

Each of these oxidation products will have a certain effect on the properties of the oil. The extent to which this occurs will depend upon the amount and nature of the individual products. This will in turn depend upon the chemical structure of the oil, and in the case of chloroform insolubles it will depend also on the characteristics of the engine.

The work carried out consisted of deteriorating certain oils by (a) air-blowing through hot samples, and (b) deteriorating the same oils in a Pelapone I.C. engine, and investigating the following:

(i) the effect of the chemical structure of the oil on the extent to which oxidation occurs;

(ii) the effect of the various oxidation products on the properties of the oil;

(iii) the properties of the products of oxidation;

(iv) comparison of the oxidation products and their effects on

the properties of the oil in the two methods of oxidation.

CHAPTER V

CHAPTER V.

Characteristics of Fuel and Oils Used

Four refined mineral lubricating oils containing no additives were used in the present work. Table I gives the place of origin and refining history of each oil, and Table 2 gives the refractive index, density, molecular weight and viscosity as determined by the methods described in detail in the Appendix. Since the oils were found to contain little or no sulphur the sulphur content was ignored and the resulting n-d-M analyses of the oils given in Table 3.

The fuel used in the engine tests was an unleaded gasoline the characteristics of which are given in Table 4.

TABLE I.

	PLACE OF ORIGIN	REFINING HISTORY
OIL NO.1.	Mid-continent	Acid refined, M.E.K. - solvent extracted and clay filtered.
OIL NO.2.	Middle East	Middle distillate which had been phenol extracted, propane dewaxed, clay treated, vacuum re-run and bright stock added. Bright stock had been treated in a similar manner.
OIL NO.3.	Middle East	Compounded distillate and bright stock. Both distillate and bright stock were solvent extracted, solvent dewaxed and clay filtered.
OIL NO.4	Venezuela	A naphthenic feed-stock which had been vacuum distilled, caustic soda treated and re-distilled.

TABLE II.

SAMPLE	REFRACTIVE INDEX AT 20°C.	DENSITY AT 20°C. (gm/ml)	MOLECULAR WEIGHT	VISCOSITY AT 20°C. (Centistokes)
1.	1.4859	0.8830	525	364.2
2.	1.4868	0.8800	578	517.0
3.	1.5019	0.9057	523	799.1
4.	1.5280	0.9408	410	1080.3

TABLE III.

SAMPLE	$\%C_A$	$\%C_R$	$\%C_N$	$\%C_P$	R_A	R_N	R_T
1.	3.8	35.5	31.7	64.5	0.22	2.64	2.86
2.	6.7	30.5	23.8	69.5	0.46	2.06	2.66
3.	12.5	39.5	27.0	60.5	0.81	2.42	3.23
4.	27.5	49.8	22.3	50.2	1.42	1.77	3.19

TABLE IV

CHARACTERISTICS	VALUE	I.P. TEST NUMBER	A.S.T.M. TEST NUMBER
Specific gravity at 60/60°F.	0.7257	160	D1298
Distillation:		123	D86
10% evaporation at, °C.	85		
50% " " °C.	119		
90. " " °C.	145		
FBP " " °C.	187		
Residue, % Vol.	1		
Abel flash point, °F.	67	33/59	
Reid vapour pressure p.s.i.g.	7.6	69	D323
Octane number, MM	80	44	D357
RM	87	126	D908
Gum, mg/100ml.	2	38	D381
Sulphur, %wt.	0.12	107	D90
Corrosion	0.5	154	D130
TEL content, ml/IG	0	116	D526
Oxidation stability, min.	475	40	D525

CHAPTER VI

CHAPTER VI

1. Institute of Petroleum Oxidation Test

Earlier work in this laboratory used the Institute of Petroleum Test I.P. 48 (87,88) as a method of oxidising various oils, since this test has the advantage of both being a standard test and providing operating conditions which are easy to control. In the earlier stages of the present work this test was used to oxidise some of the oils used and to provide a basis of correlation between all the oils used in this work, some of which had been oxidised previously (87,88).

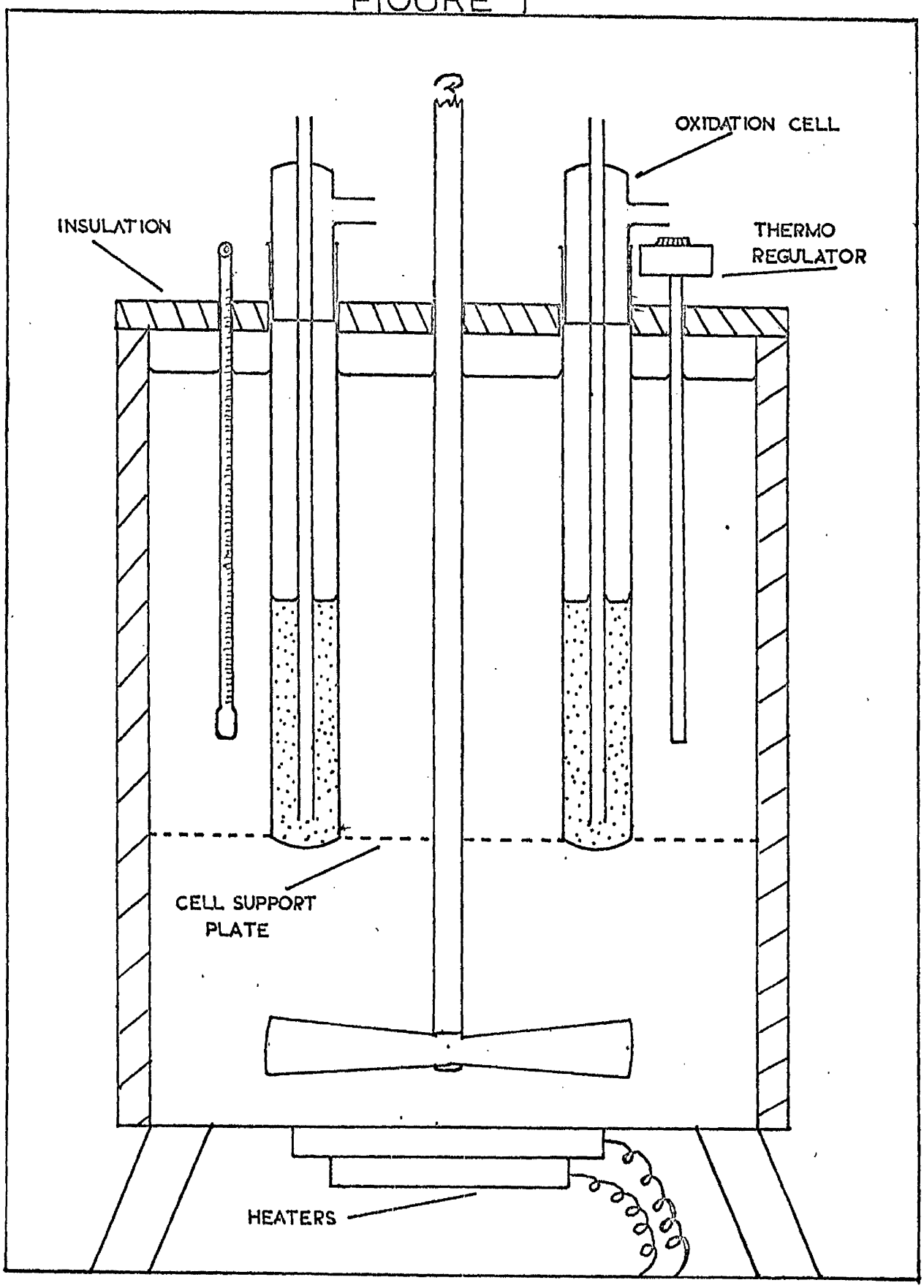
In the Institute of Petroleum Test air is passed through a 40ml. oil sample, kept at 200°C., at a rate of 15 litres/hour for a period of 6 hours. The sample is then left for 12 to 18 hours and oxidised for a further 6 hours, giving a total oxidation time of 12 hours.

Ramsbottom carbon residue and kinematic viscosity at 100°F. are measured before and after oxidation. Oxidation of the oil is measured by taking the ratio of viscosity after oxidation to viscosity before oxidation, and the increase in percentage carbon residue.

This test was intended to enable oils to be arranged in order of stability, but in this laboratory has been modified so that oils can be oxidised for varying periods of time under constant conditions. It has been shown (87) that there is no essential difference between oxidising oils for one prolonged period and for 6 hour periods as in the standard test.

The apparatus employed in the I.P. test consisted essentially of a heat resistant glass boiling tube (25cm. long, 2.5cm. diameter) with a

FIGURE 1



OXIDATION APPARATUS.

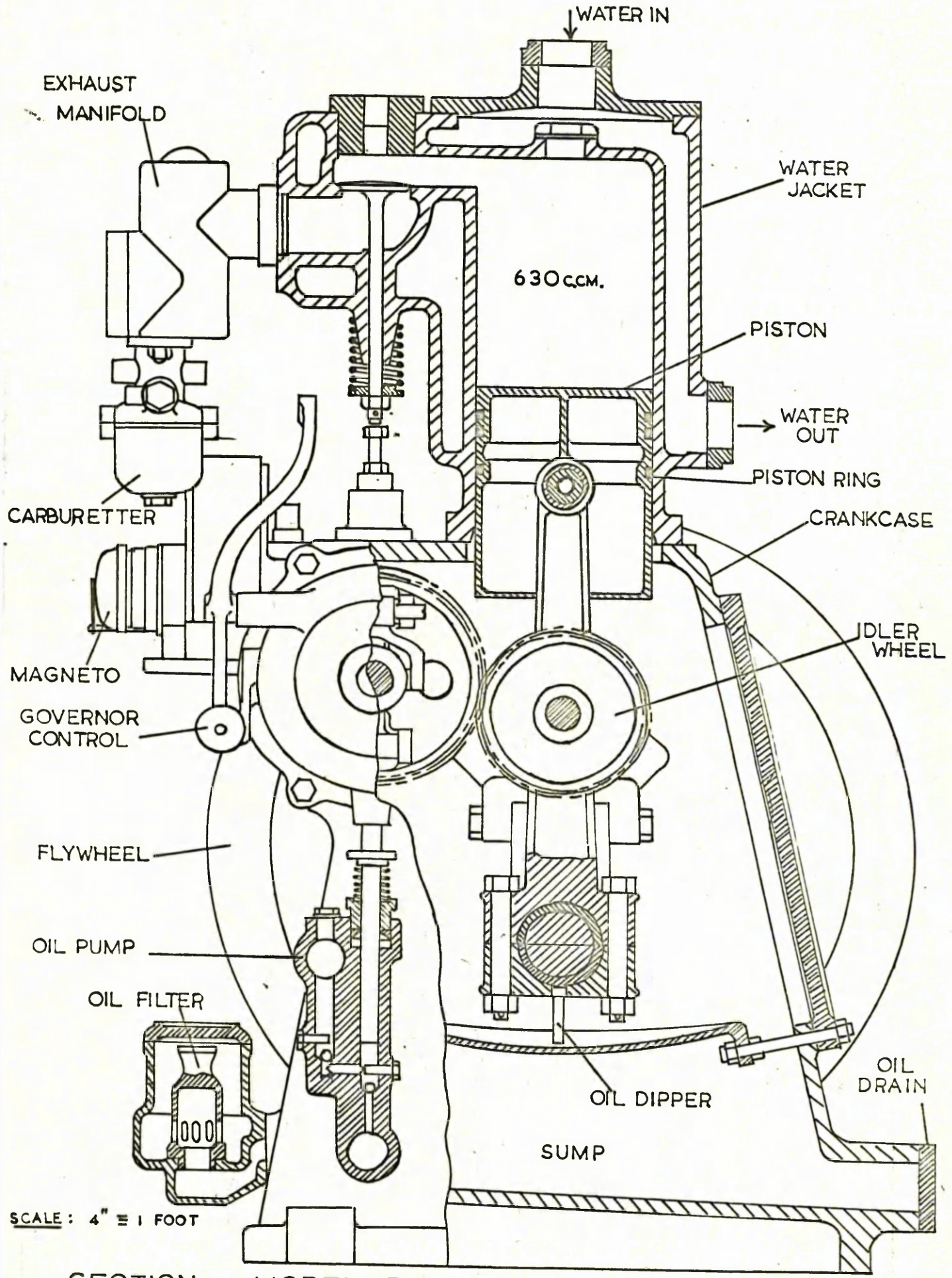
ground glass top fitted with a glass cap through which passed a glass air inlet tube and an air outlet tube. The inlet tube went to within 4mm. of the bottom of the boiling tube which was graduated to contain 40ml. of oil at room temperature.

The heating bath consisted of a copper tank (22.5cm. diam., 30cm. deep) filled with a heavy-duty heating oil. At a depth of 22cm. there was a perforated brass plate which acted as a support for the four oxidation cells. A hard asbestos lid covered the bath, this lid being fitted with a thermometer and a Sunvic thermostatic control. The bath was heated externally by two electric heaters (1000 W and 800 W). The larger heater was used as a boost heater and when the required temperature was reached control was maintained using the smaller heater.

A single bladed propellor provided the necessary stirring, this propellor being fitted to a constant speed electric motor mounted above the bath. Insulation of the bath was provided by a 1 in. thick fibre glass sheath.

Non-pulsating air-flow was obtained by means of a "Proctor" diaphragm pump capable of delivering 300 cu. in. per minute. In order to gain a more sensitive flow control, V-notches were cut in the plug of the stop cock in such a way as to terminate at the hole. This made it possible to have a range of flow rate rather than the normal on-off flow associated with a glass stop cock. The flow rate was measured on a type U-tube manometric flowmeter with capillary tubing as the orifice. A flowmeter was used for each individual oxidation cell, and the four flow meters were connected to a common manifold from the "Proctor" pump.

In Fig. I. an end elevation of the bath is shown with two oxidation cells in position.



SECTION OF MODEL P.F.I. GASOLINE ENGINE

2. The Pelapone Engine

The engine used in this study was a Pelapone PF.1., manufactured by the New Pelapone Engine Co. Ltd., Wakefield, as a power generator, (see accompanying sectional drawing of engine). It was a single cylinder 4-stroke engine, with spark ignition, and which used straight-run gasoline as fuel. Stroke and bore were both equal to 4.75 ins. and cooling was achieved by means of water passing through a jacket. A generator was coupled to the engine, having a rated output of 230 V. and 12.4 A. at 1000 r.p.m., the rated horse-power of the engine at this speed being 4.5 b.h.p.

The engine was run at constant speed, 1000 r.p.m., regulated by means of a throttle governor. The cooling water rate was maintained at 1.4 gal. per min, throughout the tests, the inlet temperature being 55°F. - 60°F. and the outlet temperature 70°F. - 75°F. These temperatures were measured by means of mercury thermometers inserted in pockets in the water pipe. Although the ambient temperature ranged from 45°F - 65°F. it appeared to have no effect on the running temperature of the engine, and under these operating conditions the sump temperature measured by a thermocouple, stayed almost constant (110°F. - 115°F.). Due to the rapid oil circulation (100mp./min) in the engine, the oil in the sump reached this temperature within one-hour of starting up. Lubrication of the moving parts was achieved mainly by means of a pumping action but also partially by a splashing action.

An unleaded gasoline was used as fuel in these experiments the characteristics of which are given in Chapter V. The consumption rate of the fuel was 43ml./min. by gravity feed.

At the end of each test the oil was drained from the sump and sampled, 200ml. being taken, after about one-third of oil had run out. The sump holds

4.6 litres and was filled with this amount at the commencement of each run. No make-up was added during a test.

When sampling had been completed the sump was emptied and the entire engine was washed with 100/120° petroleum ether, by means of a hand pumping device incorporated in the engine the 100/120° petroleum ether was circulated throughout the engine without turning the engine over more than two or three times. This hand pump was also used to feed oil to the cylinder walls before the start of a test so that engine wear was reduced (89). After washing, the engine was left exposed to the atmosphere so that all the 100/120° petroleum ether evaporated off.

The first step in the start-up procedure was to fill the sump with the particular oil to be examined and hand pump it to the cylinder walls. Filling the fuel tank with unleaded gasoline was the next step, and the fuel was then gravity fed into the carburettor by depressing the needle valve. Once this was done the ignition switch was pushed over into the "ON" position and the engine turned over by hand until ignition took place.

CHAPTER VII

CHAPTER VII

Oxidation by Modified Institute of Petroleum Test

1. Oil composition and the extent of oxidation

Oxidation of oils 1,2 and 4 was carried out by means of the modified I.P. test (Chapter VI) for various periods of time up to 24 hrs. The oxidised oils were then filtered, desludged and deresined by the procedures described in the Appendix, and analysed to determine what effect oil composition and oxidation products. In this investigation the oxidation products referred to are those which have been retained by the oil.

Production of sludges and resins

The effect of oil composition on the amount of non-volatile oxidation products formed can be seen by examination of figures 2 and 3. Oil number 1 contained the smallest amount of aromatics and formed the smallest total amount of oxidation products after 24 hours. Oil number 2 was of intermediate aromaticity and formed the second greatest amount of oxidation products, with the oil of greatest aromaticity, number 4, producing the greatest amount of non-volatile products.

Soluble sludge was formed by Oil number 1, Oil number 4 formed both insoluble and soluble sludge, and Oil number 2 formed no sludge at all. One would expect the oils with the greatest aromaticity to form sludge, but here Oil number 1 has a lower aromatic content than Oil number 2 and yet forms sludge, whereas the latter forms none.

Oil number 1 did not start producing sludge until after 9 hours oxidation, and then at an increasing rate of formation. Soluble and insoluble

sludge appeared to be formed from the start by Oil number 4 and at a linear rate of formation. The rate of formation of soluble sludge by Oil number 1 was greater than that of Oil number 4, but the total amount formed was much less than that of Oil number 4 after 24 hours oxidation.

The sludge forming oils, numbers 1 and 4 produced approximately the same quantity of resins after 24 hours, but Oil number 2 produced the greatest amount of resins after this time. The rate of formation of resins by Oils 1 and 4 decreased after a time, whereas the rate of formation of resins by Oil number 2 continued to be constant. It would seem that the rate of formation of resins decreased as the formation of sludges increased. This was particularly so in the case of Oil number 1, in which sludge did not commence to appear until 9 hours oxidation which coincided with a decrease in the rate of resin formation. This effect has also been noticed in engine tests (90) in which a decrease in resin content was coincident with an increase in sludge value. This would suggest that resins are the first products of oxidation and are further oxidised to sludges.

The results shown in figures 2 and 3 are consistent with the work of Davis (90) who showed that resins are formed until a constant quantity is reached and sludges are produced at a constant rate. This is true for less refined oils, i.e. oils which contain appreciable amounts of aromatics, and would account for the behaviour of Oil number 4. Oil number 1 however has a lower aromaticity than Oil number 2 and yet produces sludge. This may well be due to an optimum aromaticity effect as mentioned earlier (86,87,88).

Only in the case of Oil number 1 was the rate of formation of sludge found to be approximately equal to the decrease in the rate of formation of

FIGURE 2

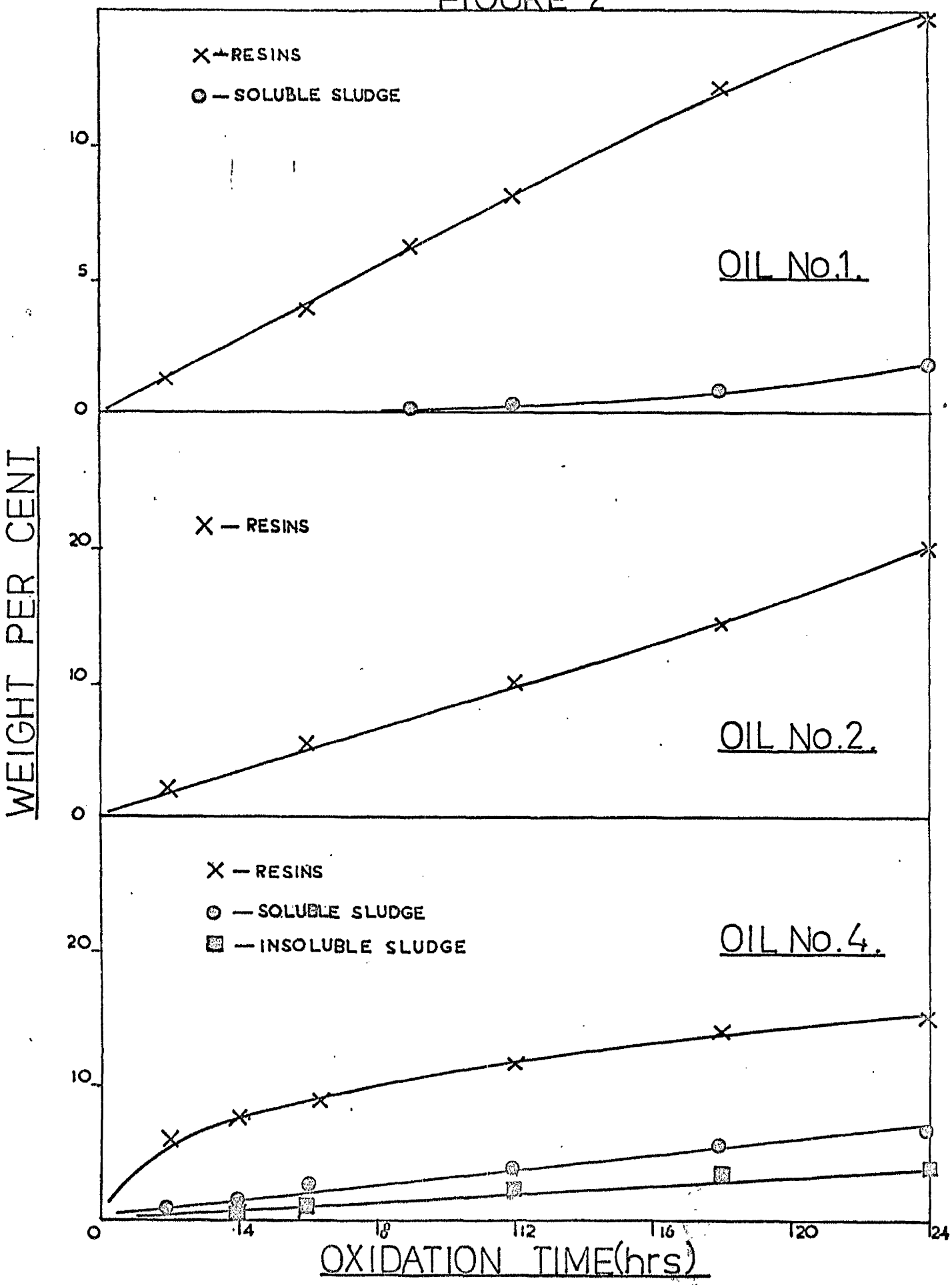
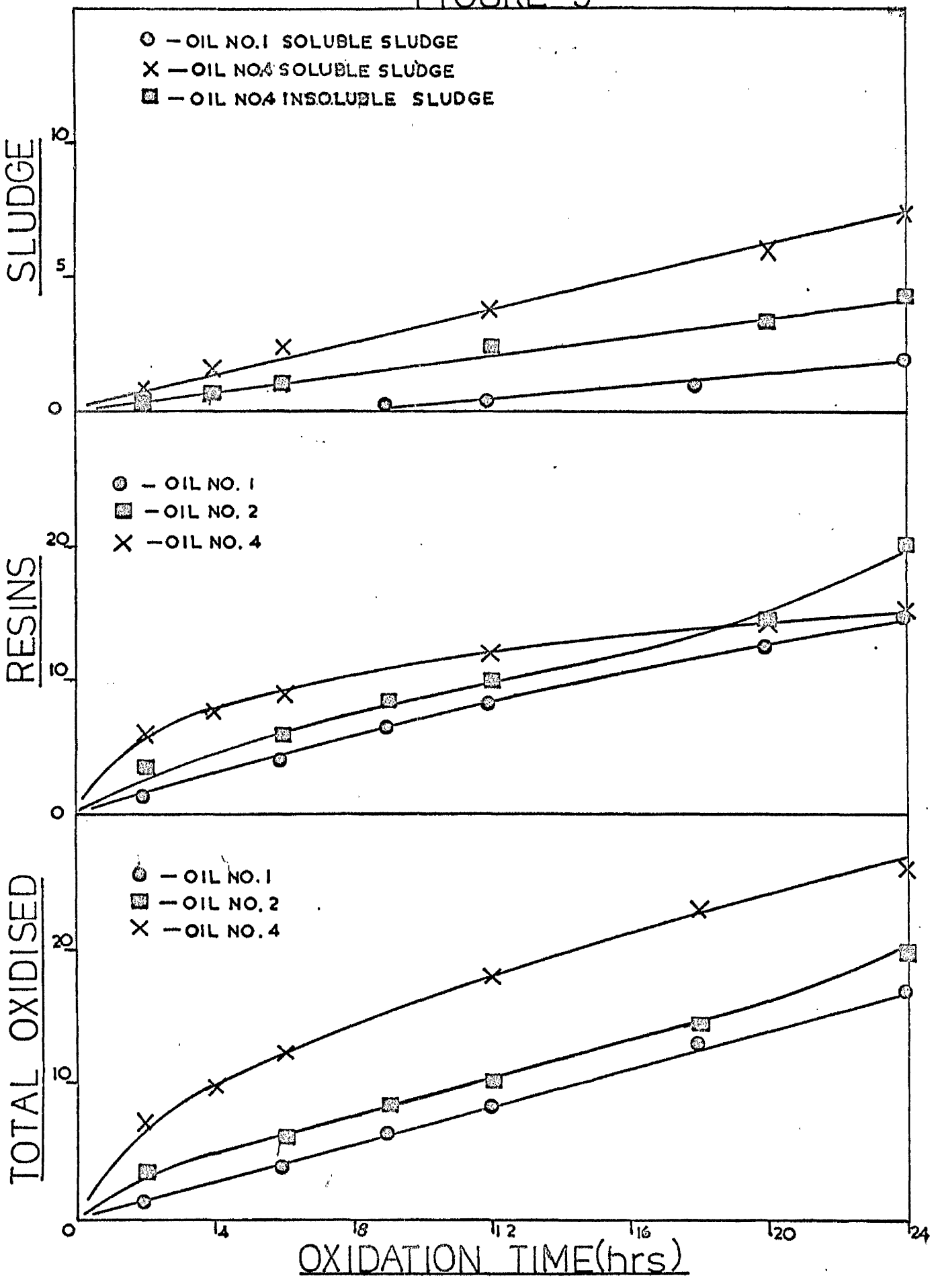

X — RESINS
O — SOLUBLE SLUDGE
OIL No.1.
X — RESINS
OIL No.2.
X — RESINS
O — SOLUBLE SLUDGE
INSOLUBLE SLUDGE
OIL No.4.
WEIGHT PER CENT
0
5
10
20
10
20
10
0
4
8
12
16
20
24
OXIDATION TIME(hrs)

FIGURE 3


O — OIL NO.1 SOLUBLE SLUDGE
X — OIL NO.4 SOLUBLE SLUDGE
▣ — OIL NO.4 INSOLUBLE SLUDGE
SLUDGE
0
5
10
O — OIL NO. 1
▣ — OIL NO. 2
X — OIL NO. 4
RESINS
0
10
20
O — OIL NO. 1
▣ — OIL NO. 2
X — OIL NO. 4
TOTAL OXIDISED
0
10
20
4
8
12
16
20
24
OXIDATION TIME(hrs)

the resins. This was not so for Oil number 4 and the descrepancy may be due to an increase in the formation of volatile products, such as water and carbon dioxide, not determined in this investigation.

The cyclic theory of sludge precipitation, in which resins are oxidised to sludge until the limit of oil solubility is reached when they precipitate carrying down absorbed resins, the resin content then increasing to a new maximum and the cycle repeated, does not appear to apply in the above cases of oil oxidation.

Acid formation

Oils which have been oxidised possess an "acidity" due to products which are a great deal more complex than simple acids and esters (91). These alkali consuming substances include lactones and polyhydroxy compounds, but in the present investigation "acids" were regarded as oxygenated compounds capable of producing hydrogen ions and did not include carbonyl compounds. This was done because no relationship has yet been found between corrosion and neutralisation or saponification numbers (91).

From figure 4 it can be seen that the acidity of all three oils increases with oxidation time, but that the increase is linear for Oil number 1, whereas Oils 2 and 4 have an increasing rate of formation. When sludge is removed, either by filtration or by pentane treatment, the acidity decreases considerably, indicating that the sludges have a high acid number. When resins are removed the acidity is reduced to the value obtained for the unoxidised oil.

It would appear from figure 4 that the total acidity produced after 24 hours oxidation is dependant on the aromatic content - the greater the

FIGURE 4

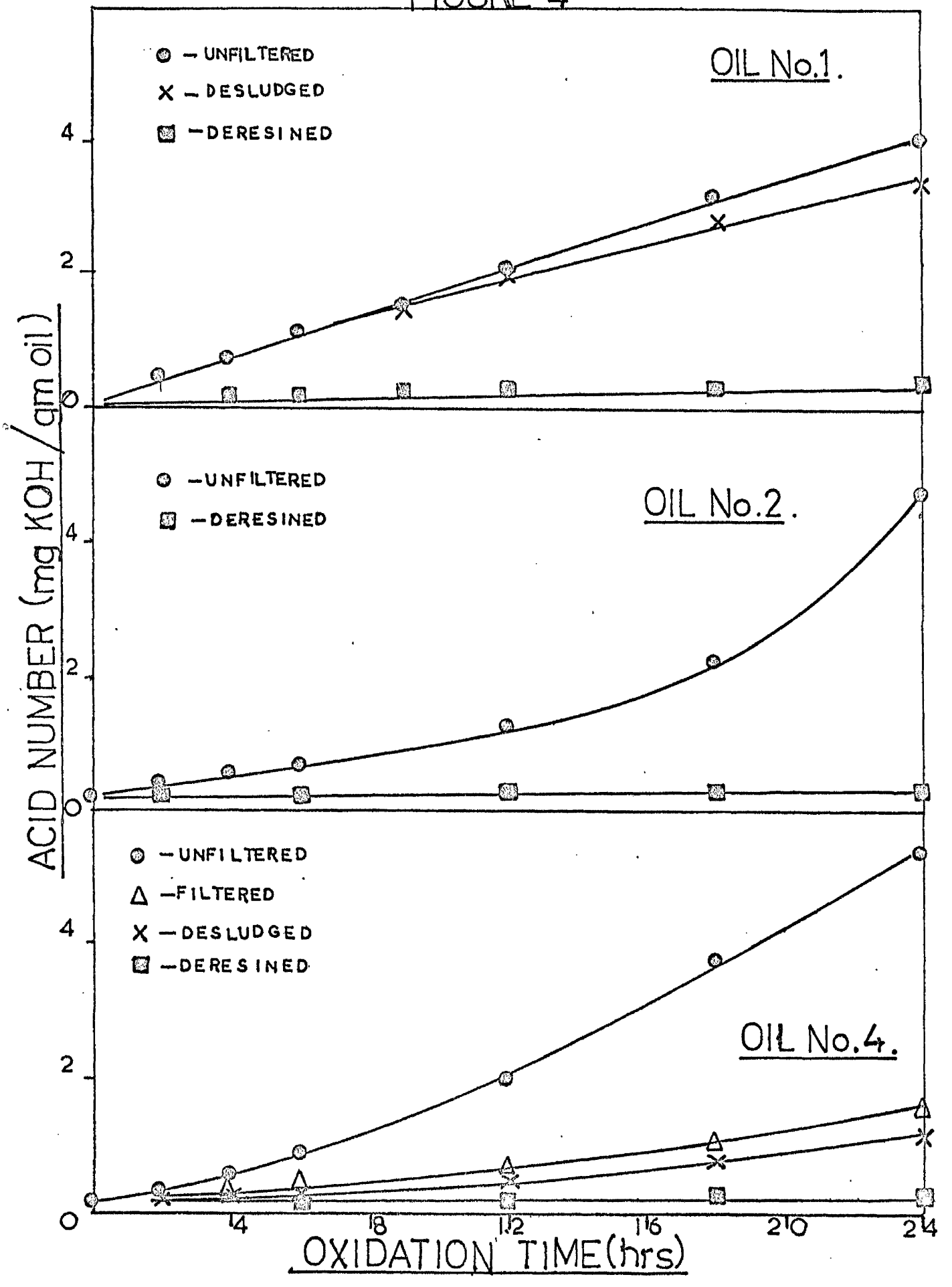
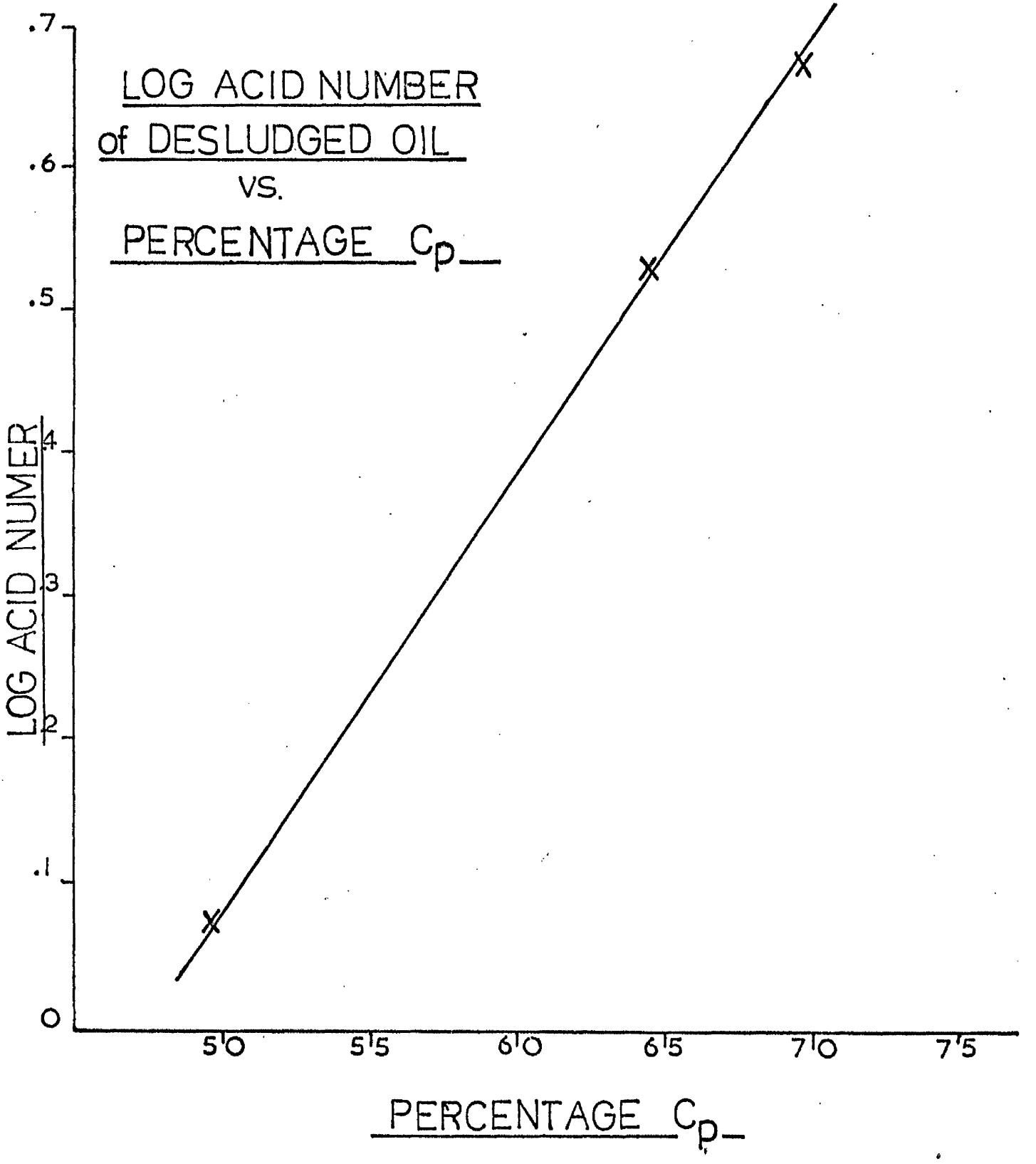

OIL No.1.
— UNFILTERED
— DESLUDGED
— DERESINED
OIL No.2.
— UNFILTERED
— DERESINED
OIL No.4.
— UNFILTERED
— FILTERED
— DESLUDGED
— DERESINED
ACID NUMBER (mg KOH / gm oil)
0
2
4
1/4
1/8
1/2
1/6
2/0
2/4
OXIDATION TIME (hrs)

FIGURE 5.


LOG ACID NUMBER
of DESLUDGED OIL
VS.
PERCENTAGE C_p
LOG ACID NUMER
.7
.6
.5
.4
.3
.2
.1
0
5'0
5'5
6'0
6'5
7'0
7'5
PERCENTAGE C_p

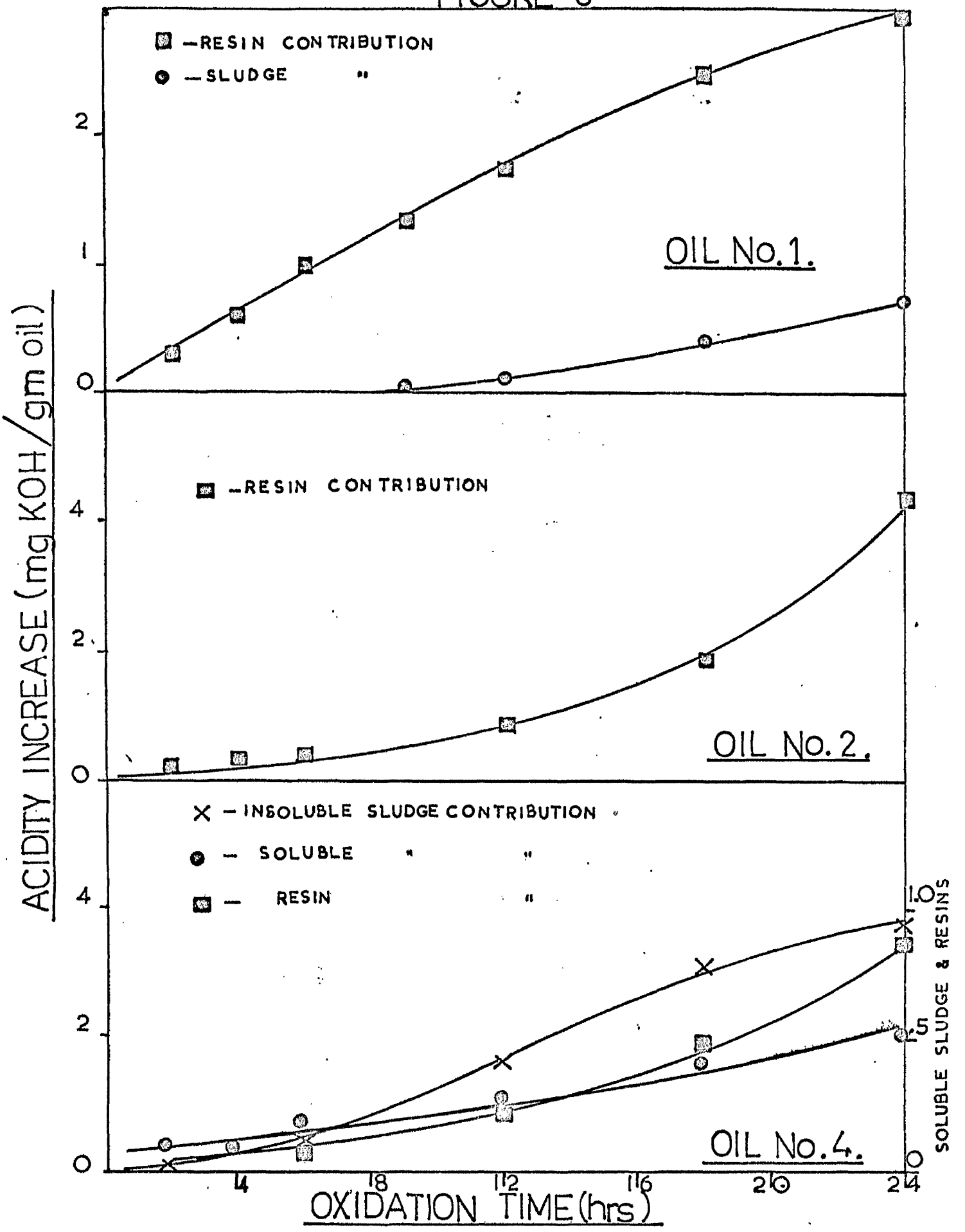
aromaticity then the greater the acidity. Larsen (92) on the other hand, found no apparent trend in the total acidity formed by oils from different sources. According to Gibson (87) and Beaton (88), however, there is a linear relationship between the logarithm of the acid number of the desludged oil and the percentage carbon in the paraffinic structure of the original oil. This was plotted for Oils, 1, 2 and 4 at 24 hours and that such a linear relationship exists can be seen from figure 5. Therefore, it would appear that the acidity of the non-sludging part of the oil is related to the percentage paraffins in the original oil, and that the total acidity is related to the sludge forming tendencies of the oil.

Figure 6 shows what contribution insoluble sludge, soluble sludge and resins each make to the increase in acidity as oxidation progresses. The rate of increase in acidity due to resins in Oil number 1 is linear up to 9 hours and then the rate began to decrease. This was coincident with the formation of soluble sludge, at an increasing rate, which also contributed to the total acidity.

Acidity increase in Oil number 2 was due solely to the formation of resins, and hence the plot of acidity increase due to resins against oxidation time is similar to that in figure 2 for total acidity against time. This shows the rate of acidity increase to be increasing with oxidation time.

In the initial stages of oxidation of Oil number 4 all three oxidation products contributed almost equally to the total acidity, thereafter the bulk of the increase being due to the production of insoluble sludge. Up until about 16 hours oxidation the soluble sludge contributed slightly more to the total acidity than the resins did, but after 16 hours the resins gave more than the soluble sludge to the overall acidity.

FIGURE 6


—RESIN CONTRIBUTION
—SLUDGE "
OIL No.1.
—RESIN CONTRIBUTION
OIL No.2.
× — INSOLUBLE SLUDGE CONTRIBUTION
— SOLUBLE " "
— RESIN "
OIL No.4.
ACIDITY INCREASE (mg KOH/gm oil)
SOLUBLE SLUDGE & RESINS
OXIDATION TIME (hrs)
0
1
2
4
1.0
1.5
4
8
12
16
20
24

Much thought has been given to the formation of sludge and acidity during oxidation, and it is now known that highly refined oils rapidly increase in acidity when oxidised and that sludge formation is often association with a decrease in the acidity of the remaining oil. It has been suggested that acids were the precursors of sludges and resins (93) and that sludge formation was due to condensation of acidic materials with polycyclic naphthenes. This theory can be discounted, however, since paraffinic type oils can product large amounts of acid without the formation of sludge, e.g. Oil number 2.

More recent theories are that aldehydes and ketones precede the formation of sludge (94) and that the sludge itself is produced by the condensation of aromatic hydroxyl compounds with carbonyl compounds (95). If this is the correct manner in which sludge is produced then the formation of acids and sludge should be competitive since they would both be formed from carbonyl compounds.

Oxidation of transformer oils showed that where the rate of acidity formation decreased, the rate of sludge formation increased. Under the particular oxidation conditions the diffusion of oxygen was the rate controlling factor. The results were explained by assuming that the acidic components in the oil partially represented potential sludge since the sludge formed later in the oxidation was of high acidity.

There can be no doubt that there is some relationship between acidity and sludge formation, but the actual nature of this relationship is still uncertain. Insoluble sludge formed during the course of the present work had greater acid values than those of the soluble sludge or resins, and the insolubility of this sludge may be connected with its highly polar acid groupings.

It may be the case that the soluble sludge continues to be oxidised until its acidity is such that it is no longer soluble in the non-polar oil and is therefore precipitated as insoluble sludge.

Carbon residue

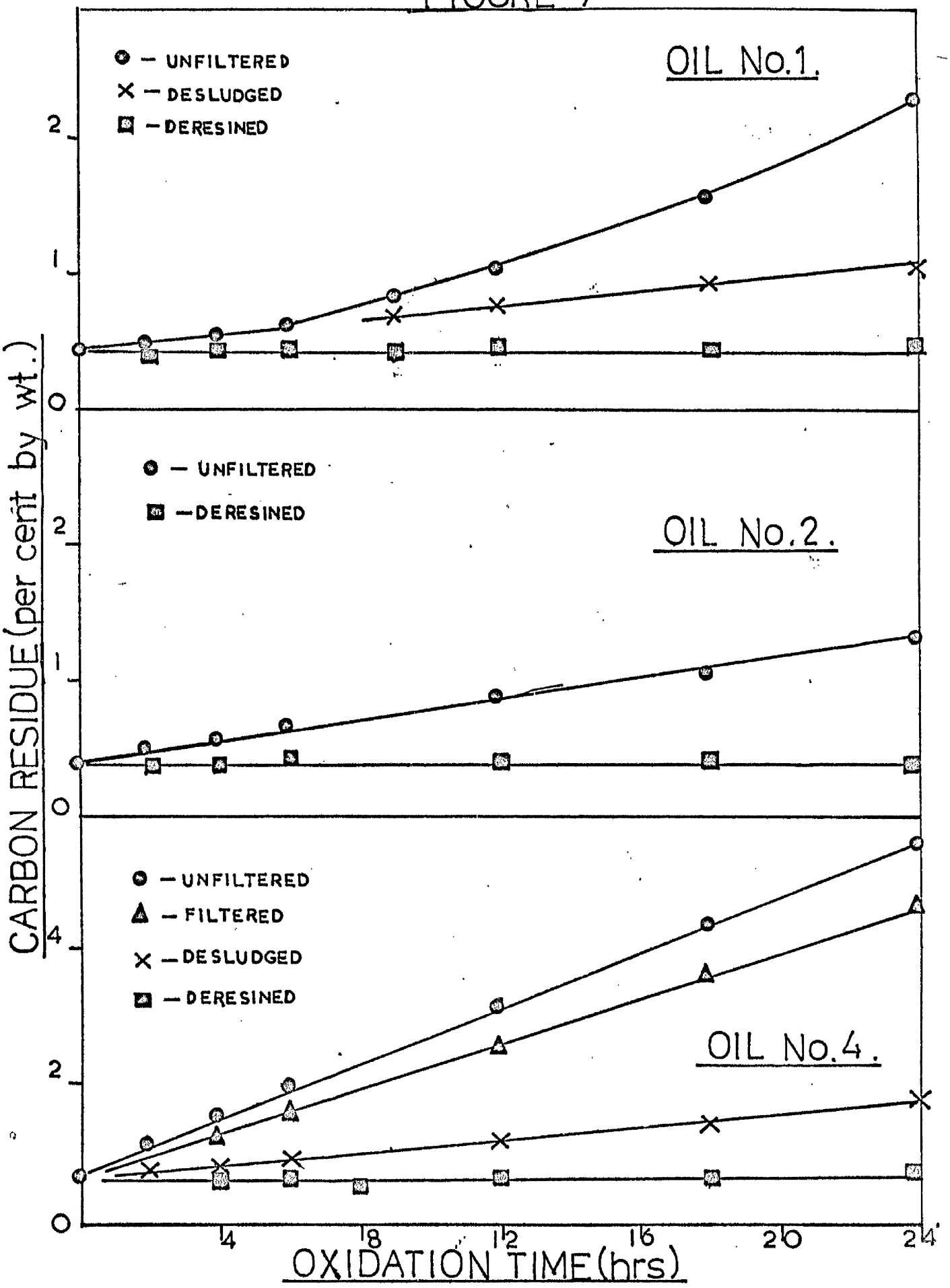
With increasing oxidation time the carbon residues of all three oils increased (figure 7). The rate of increase in carbon residue of Oil number 1 was linear up to 9 hours oxidation, but after this time the rate of formation increased with oxidation time. It would seem therefore that soluble sludge has a large carbon residue since the formation of this sludge brought about such a sharp increase in carbon residue.

Oil number 2, which produced no sludge, exhibited a linear rate of increase in carbon residue as did Oil number 4 which produced both types of sludge. From the results obtained for Oil number 4 it is apparent that the soluble sludge had a greater carbon residue than the insoluble sludge, which in turn had a greater carbon residue than the resins.

In all three cases the carbon residues of the deresined oils were in the same range of values as that of the original oils.

The carbon residue of an oil is dependant upon its carbon/hydrogen ratio and upon its oxygen content. As oxidation proceeds the carbon/hydrogen ratio increases due to condensation and polymerisation. An increase in oxygen content causes the carbon residue to decrease, and hence the carbon residue of an oxidised oil depends both upon the chemical composition of the original oil and its oxidation behaviour. It has been shown (88) that the structure of the oxidised part of the oil and the type of reaction required to

FIGURE 7


OIL No.1.
UNFILTERED
DESLUDGED
DERESINED
OIL No.2.
UNFILTERED
DERESINED
OIL No.4.
UNFILTERED
FILTERED
DESLUDGED
DERESINED
CARBON RESIDUE (per cent by wt.)
OXIDATION TIME (hrs)
0
2
1
0
2
1
0
4
2
0
4
8
12
16
20
24

produce this structure are more important than oxygen content in determining the carbon residue of the oxidised oil. This is supported by the evidence shown in figure 7 since one would expect the more aromatic oils to have the greatest increase in carbon residue but here the increase in carbon residue depends upon whether or not the oil forms sludge during oxidation. Gibson (87) found that above 9% C_A the increase in carbon residue was a function of percentage C_A but in this work no relationship was found between increase in carbon residue and percentage carbon in the aromatic structure.

Figure 8 and 9 show the contribution of the various oxidation products to the total carbon residue of the oxidised oils. In all cases the contribution of each fraction tended towards a constant value. The order of contribution was soluble sludge > resins > insoluble sludge > hydrocarbons.

According to the work done by Vassilieff (96) the resins present in crude oils produce 20% and sludges 70% of the coke formed in the Conradson test. Oil number 1 produced soluble sludge which tended to 52% contribution, and the soluble sludge in Oil number 4 also tended to this value with insoluble sludge contributing 15%. The contribution of total sludge to the carbon residue in Oil number 4 was 67% which compared favourably with the value determined by Vassilieff. Where no sludge was formed, Oil number 2, the resin contribution tended towards 70% and where only soluble sludge was formed the resin contribution tended towards 25%. Only where soluble and insoluble sludge were formed did the resin contribution to the total carbon residue tend towards 20%.

FIGURE 8

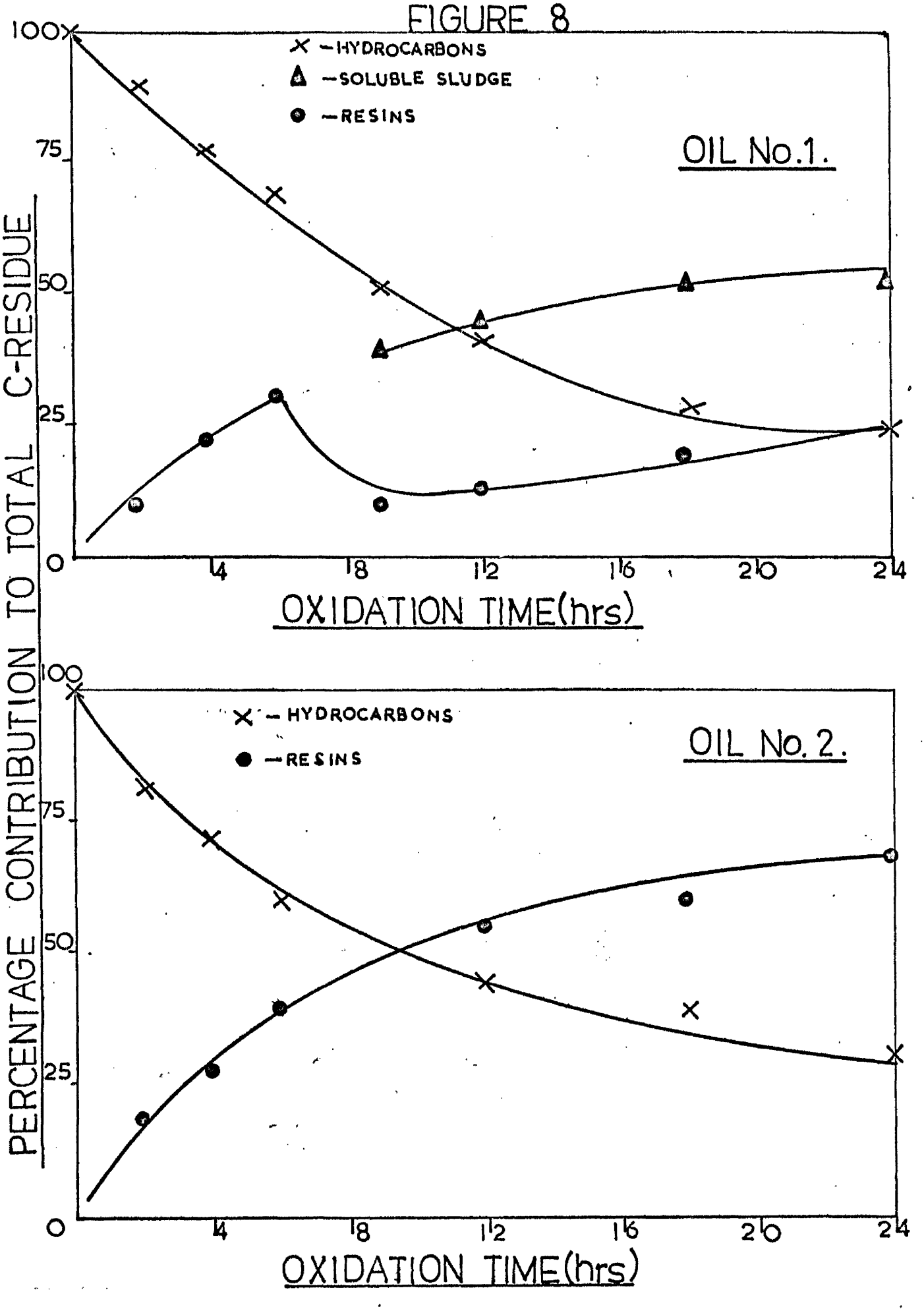
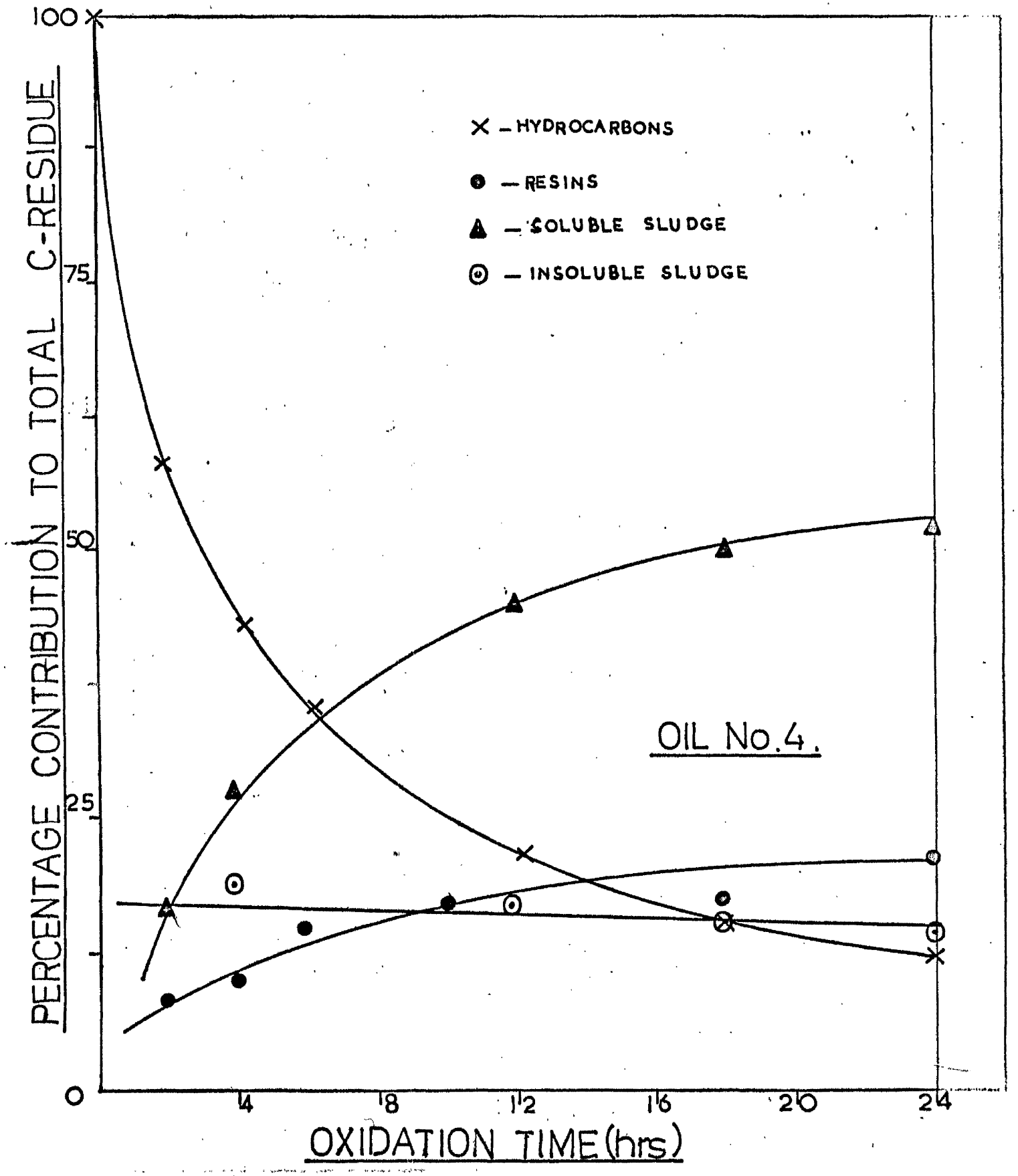

PERCENTAGE CONTRIBUTION TO TOTAL C-RESIDUE
100
75
50
25
0
× – HYDROCARBONS
▲ – SOLUBLE SLUDGE
● – RESINS
OIL No.1.
4
8
12
16
20
24
OXIDATION TIME(hrs)
100
75
50
25
0
× – HYDROCARBONS
● – RESINS
OIL No. 2.
4
8
12
16
20
24
OXIDATION TIME(hrs)

FIGURE 9


100
75
50
25
0
PERCENTAGE CONTRIBUTION TO TOTAL C-RESIDUE
× – HYDROCARBONS
● – RESINS
▲ – SOLUBLE SLUDGE
⊙ – INSOLUBLE SLUDGE
OIL No.4.
4
8
12
16
20
24
OXIDATION TIME (hrs)

2. Effect of oxidation on the characteristics of the oil

Density

Oxidation of all three oils causes an increase in density as shown in figure 10, the rate of increase in Oils 1 and 4 gradually diminishing whereas Oil number 2 shows an increasing rate of formation of denser material. This is consistent with figures 2 and 3 showing the rate of formation of retained oxidation products.

The fact that density increased in such a way suggests that the bulk of retained oxidation products are of higher density than the original oil, the less dense oxidation products probably being volatile ones such as carbon dioxide and water.

Desludging and deresining the oxidised oils decreased the density considerably. Removal of sludges reducing the density to values only slightly above that of the original oil, whereas deresining reduces the density to values below that of the original. This decrease in density by removal of resins increases as oxidation time increases.

No relationship is apparent between the percentage increase in density and percentage C_A as was found by Beaton (88). When the density increase in all four oils, Oil number 3 being oxidised to 24 hours only, was considered some relationship was apparent between the percentage increase and the total number of rings per mean molecule of the original oil (figure 11).

Viscosity

From figure 12 it can be seen that Oil number 2 shows the least increase in viscosity after 24 hours, followed by Oil number 1, and then

FIGURE 10.

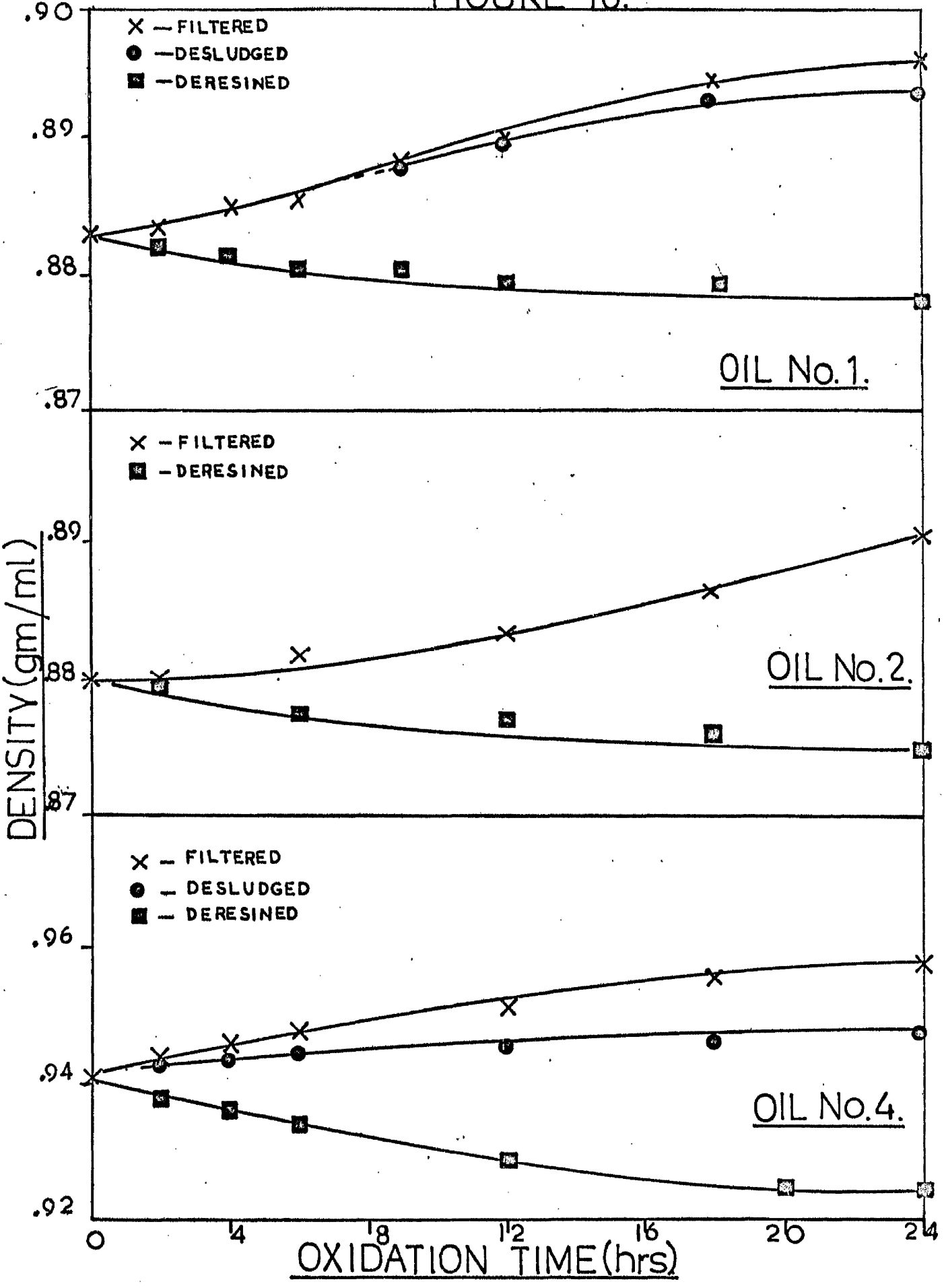

.90
.89
.88
.87
× — FILTERED
● — DESLUDGED
■ — DERESINED
OIL No. 1.
× — FILTERED
■ — DERESINED
.89
.88
.87
OIL No. 2.
× — FILTERED
● — DESLUDGED
■ — DERESINED
.96
.94
.92
OIL No. 4.
DENSITY (gm/ml)
0
4
8
12
16
20
24
OXIDATION TIME (hrs)

FIGURE 11

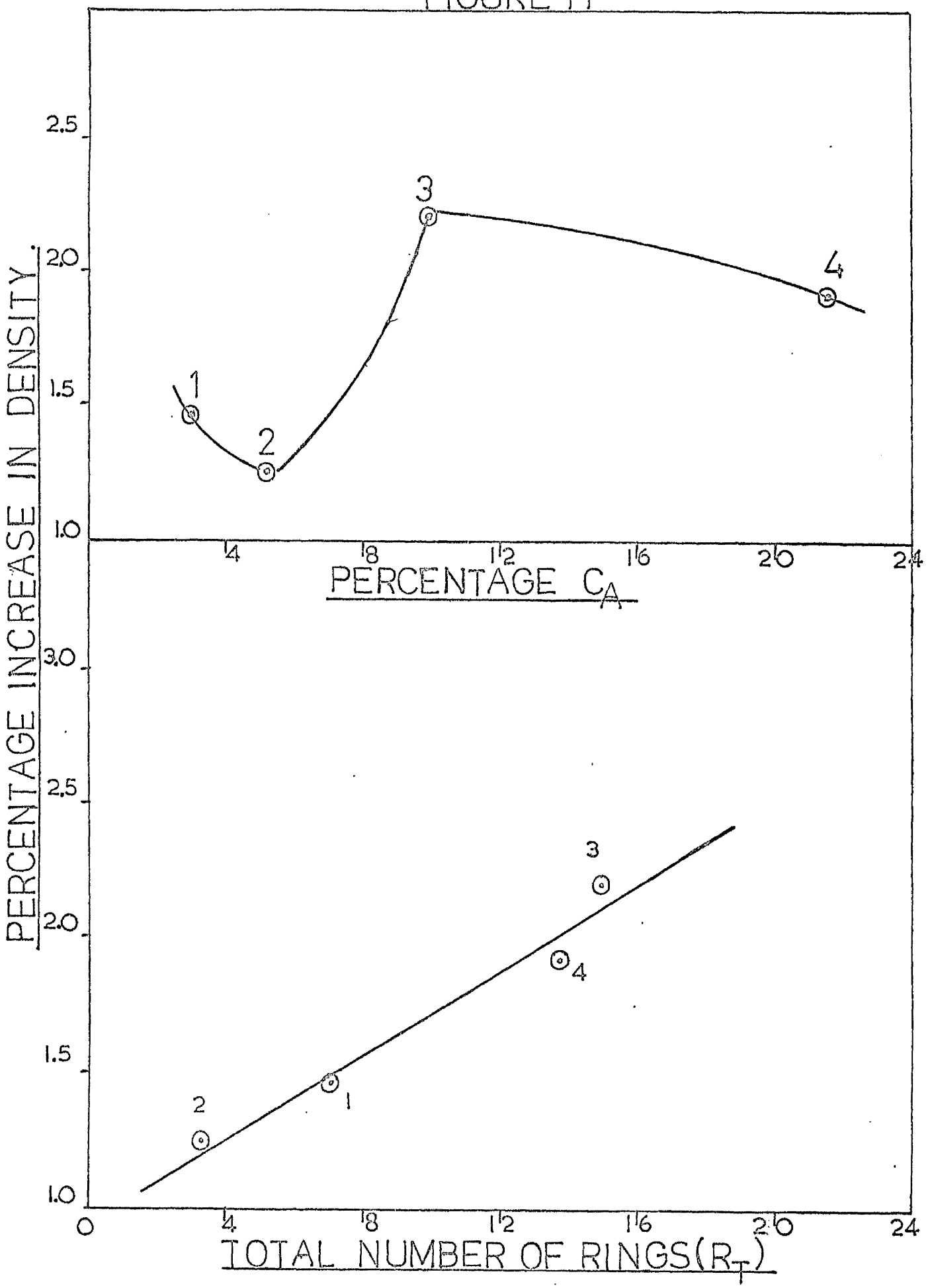
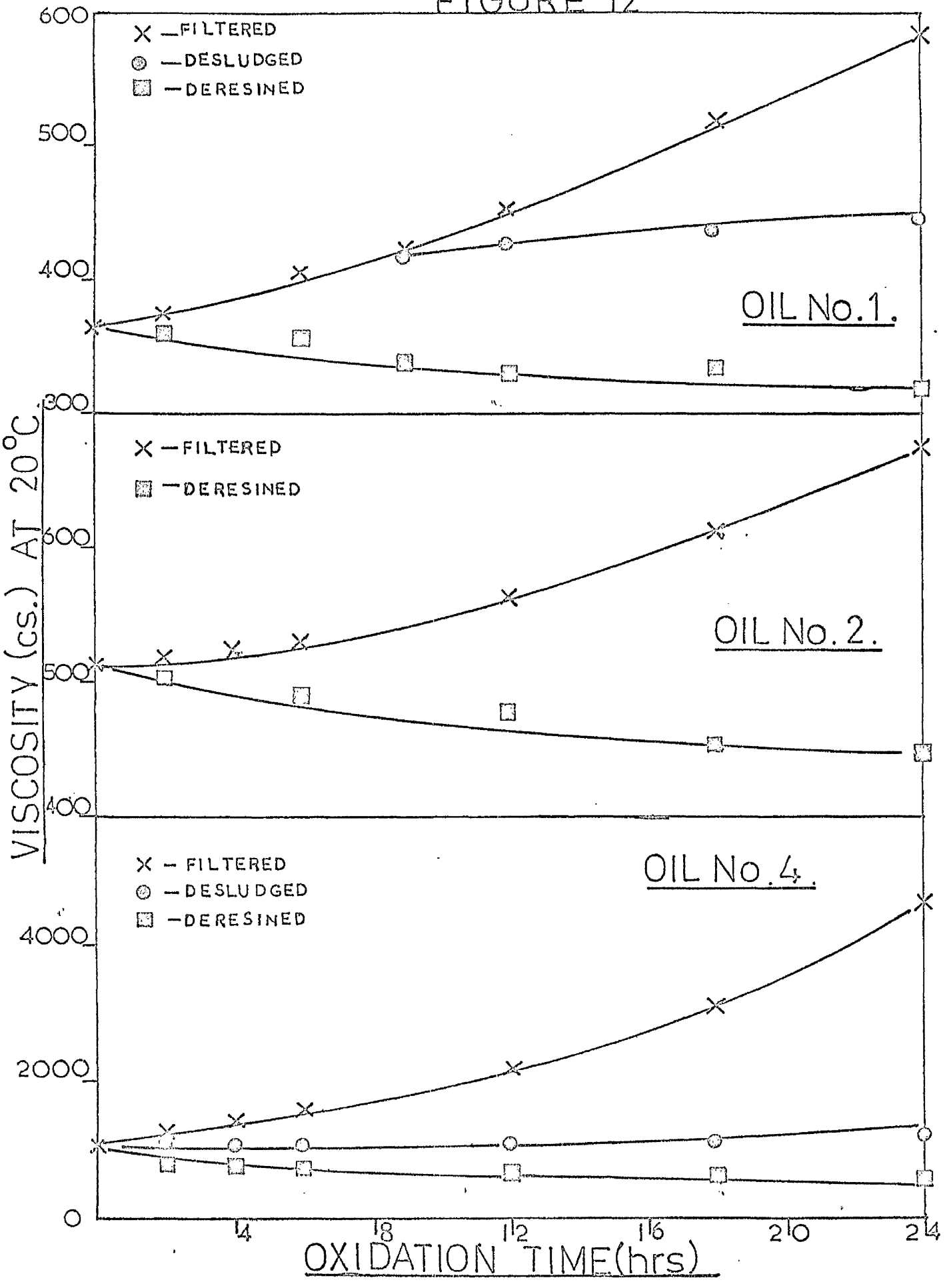

PERCENTAGE INCREASE IN DENSITY.
2.5
2.0
1.5
1.0
1
2
3
4
4
8
12
16
20
24
PERCENTAGE C_A
3.0
2.5
2.0
1.5
1.0
3
4
1
2
0
4
8
12
16
20
24
TOTAL NUMBER OF RINGS(R_T)

FIGURE 12


600
500
400
300
× —FILTERED
◎ —DESLUDGED
⊠ —DERESINED
OIL No.1.
× —FILTERED
⊠ —DERESINED
600
500
400
OIL No.2.
× — FILTERED
◎ —DESLUDGED
⊠ —DERESINED
OIL No.4.
4000
2000
0
VISCOSITY (cs.) AT 20°C.
1/4
1/8
1/2
1/6
2/0
2/4
OXIDATION TIME(hrs)

Oil number 4 which gave the greatest increase. Oils 1 and 4 are also the only two oils which formed sludges, indicating that sludges themselves have a greater viscosity than the original oils.

It would be expected that oils containing the greatest amount of aromatics would have the greatest increase in viscosity, since aromatics form oxidation products which are very viscous. But from figure 12 it can be seen that this is not necessarily the case as Oil number 2 has a greater aromatic content than Oil number 1.

In all three cases it can be seen that the rate of viscosity increase became greater with oxidation time. The Institute of Petroleum oxidation test uses the viscosity ratio after 12 hours to classify an oil with respect to its oxidation stability, but from figure 12 it can be clearly seen that this may lead to erroneous results since the rate of increase in viscosity is changing even after 24 hours oxidation. In this instance the order of viscosity ratio at 20°C. after 12 hours is the same as that after 24 hours and is also the order of oxidation stability of these three oils, i.e. Oil number 2 > Oil number 1 > Oil number 4.

Sludge removal decreased the viscosity of the oils to values just above that of the original oil, but the viscosity still increased with oxidation time. When resins were removed however the viscosity decreased to values below that of the original oil and continued to decrease as oxidation time increased.

The relative contribution of sludge and resins to the total viscosity increase in shown in figures 13 and 14. In the initial stages of the

FIGURE 13

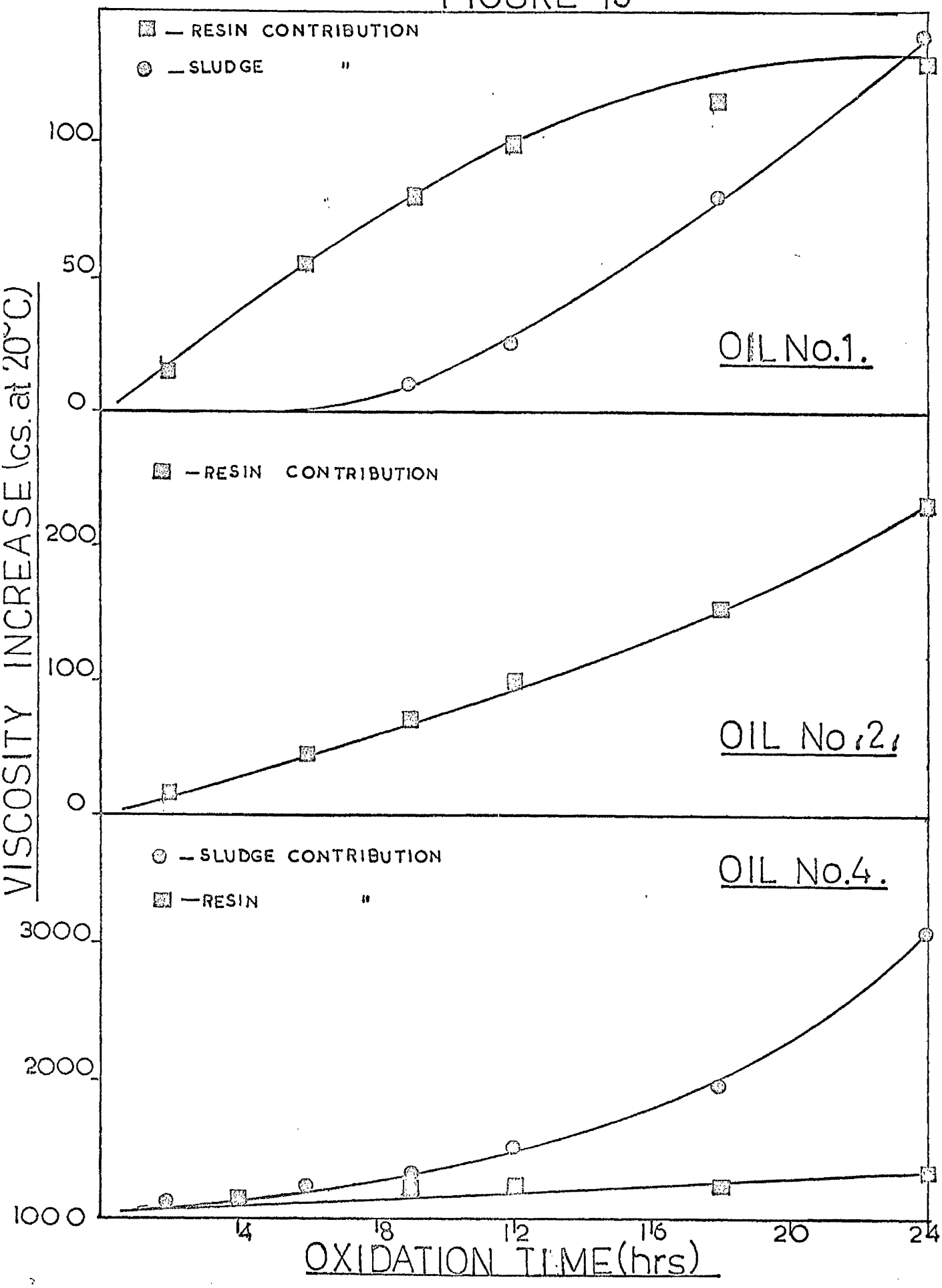
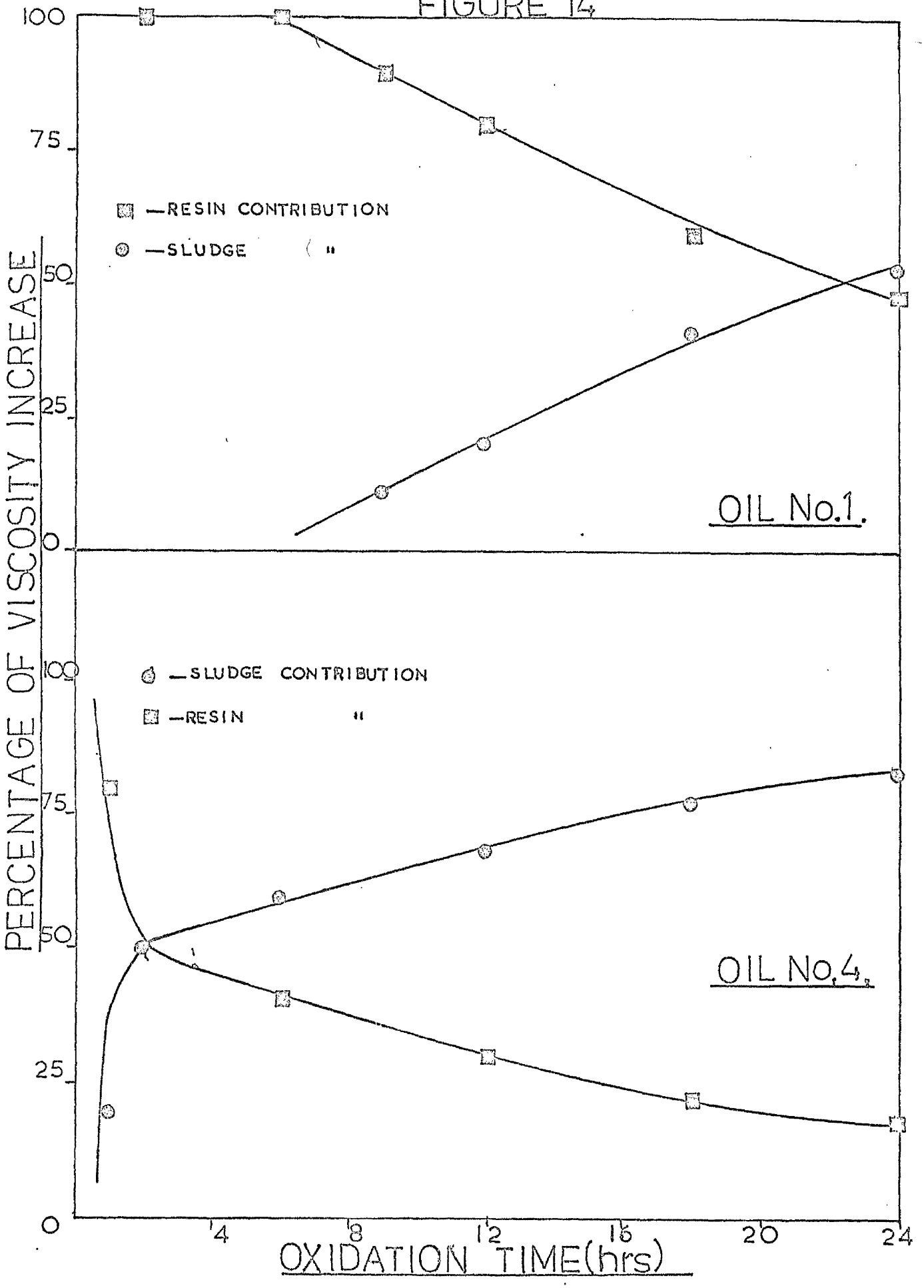

— RESIN CONTRIBUTION
— SLUDGE "
100
50
0
OIL No.1.
— RESIN CONTRIBUTION
200
100
0
OIL No.2.
— SLUDGE CONTRIBUTION
— RESIN "
OIL No.4.
3000
2000
1000
4
8
12
16
20
24
VISCOSITY INCREASE (cs. at 20°C)
OXIDATION TIME (hrs)

FIGURE 14


100
75
50
25
0
—RESIN CONTRIBUTION
—SLUDGE "
OIL No.1.
—SLUDGE CONTRIBUTION
—RESIN "
OIL No.4.
PERCENTAGE OF VISCOSITY INCREASE
4
8
12
16
20
24
OXIDATION TIME(hrs)

oxidation the contribution of the resins to the viscosity increase was in excess of the sludge contribution. In the later stages of the oxidation sludges take over the bulk of viscosity increase. It would appear then that the relative contribution of sludge and resins to the increase in viscosity depends upon their relative rates of formation.

These findings are not in agreement with those of Hicks-Bruun et al (67) who found that, in two oils of 19 and 20% aromatics, resins were responsible for 80 and 90% of the viscosity increase respectively. These workers did not oxidise the oils under such strenuous conditions as was done in present investigation, and this may be the reason for the discrepancy in results.

Fundamental Viscosity Temperature Index

The F.V.T.I. of an oil expresses the dependance of its viscosity upon temperature, and was first proposed by Cornelissen and Waterman (97,98). The F.V.T.I. is given by the logarithm of the ratio of the viscosity at 20°C. to the viscosity at 50°C. and takes the place of the standard viscosity index (V.I.) system put forward by Dean and Davis (99). The viscosity index is expressed by the formula:

$$V.I. = \frac{L - U}{L - H} \cdot 100$$

where L,H and U are the viscosities at 100°F. of a standard oil V.I. = 0, of a standard oil V.I. = 100, and of the sample under investigation respectively. The two standard oils have a viscosity at 210°F. equal to that of the unknown.

FIGURE 15

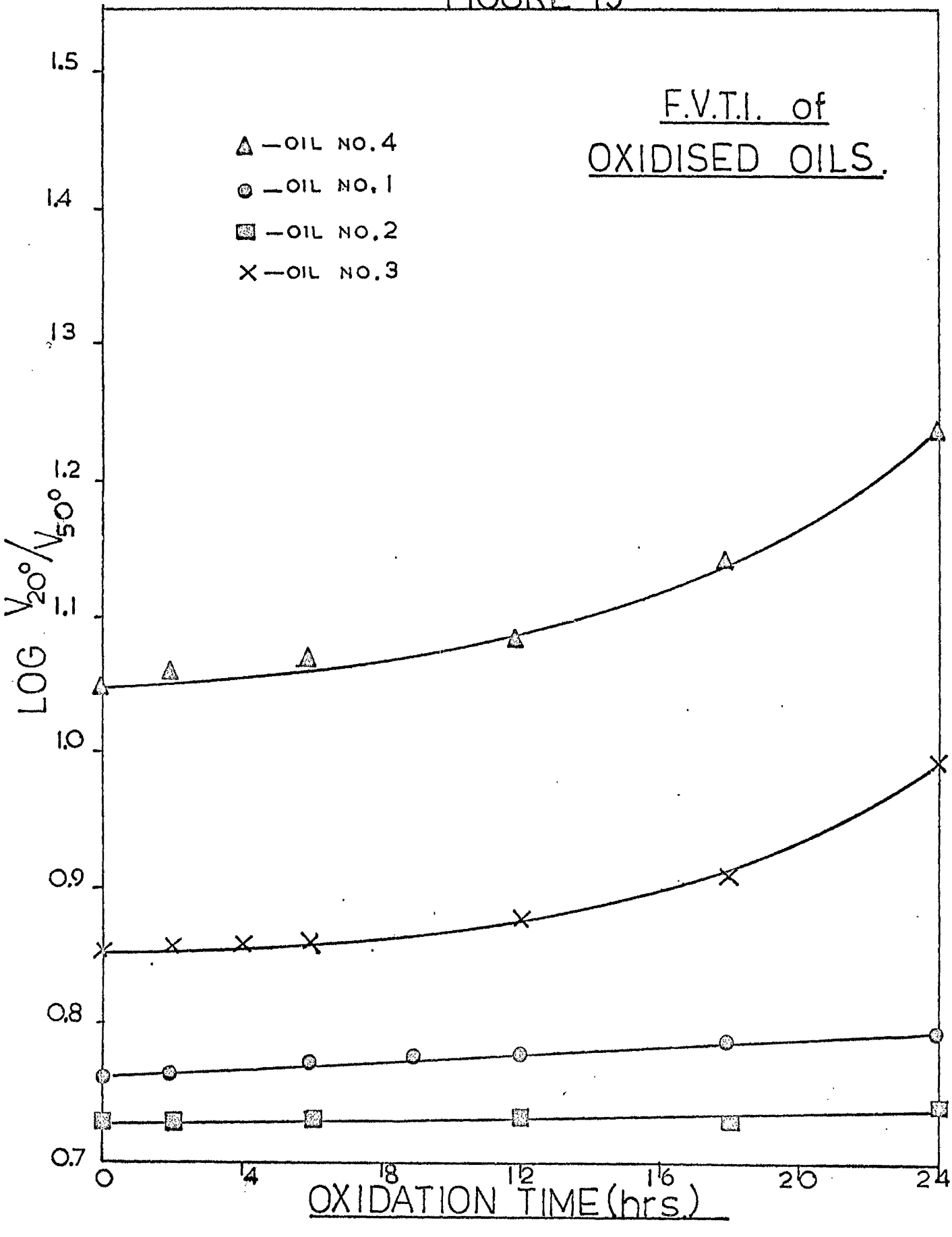

F.V.T.I. of
OXIDISED OILS.
Δ —OIL NO. 4
⊙ —OIL NO. 1
▣ —OIL NO. 2
× —OIL NO. 3
LOG V20°/V50°
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0
4
8
12
16
20
24
OXIDATION TIME (hrs.)

FIGURE 16

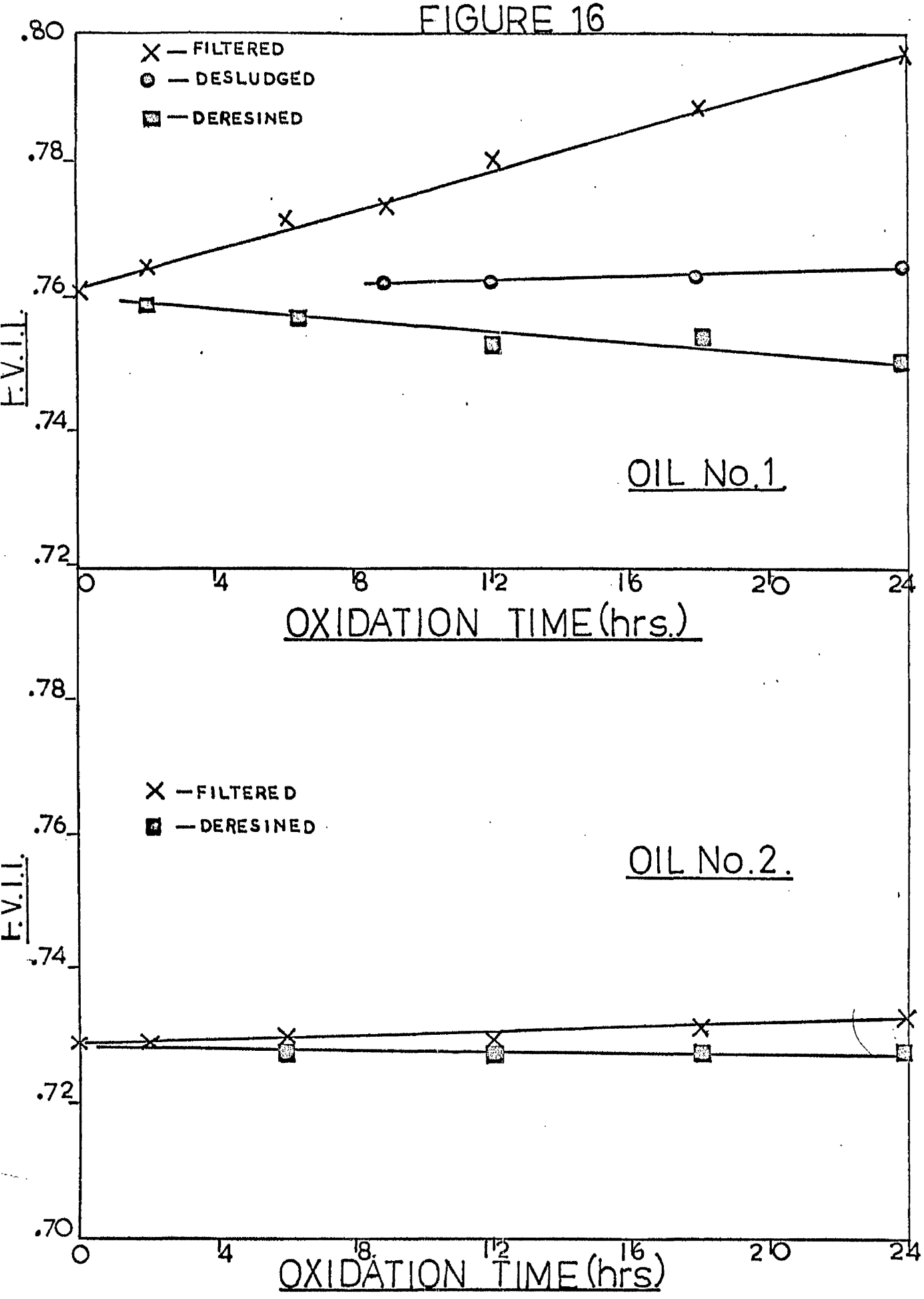
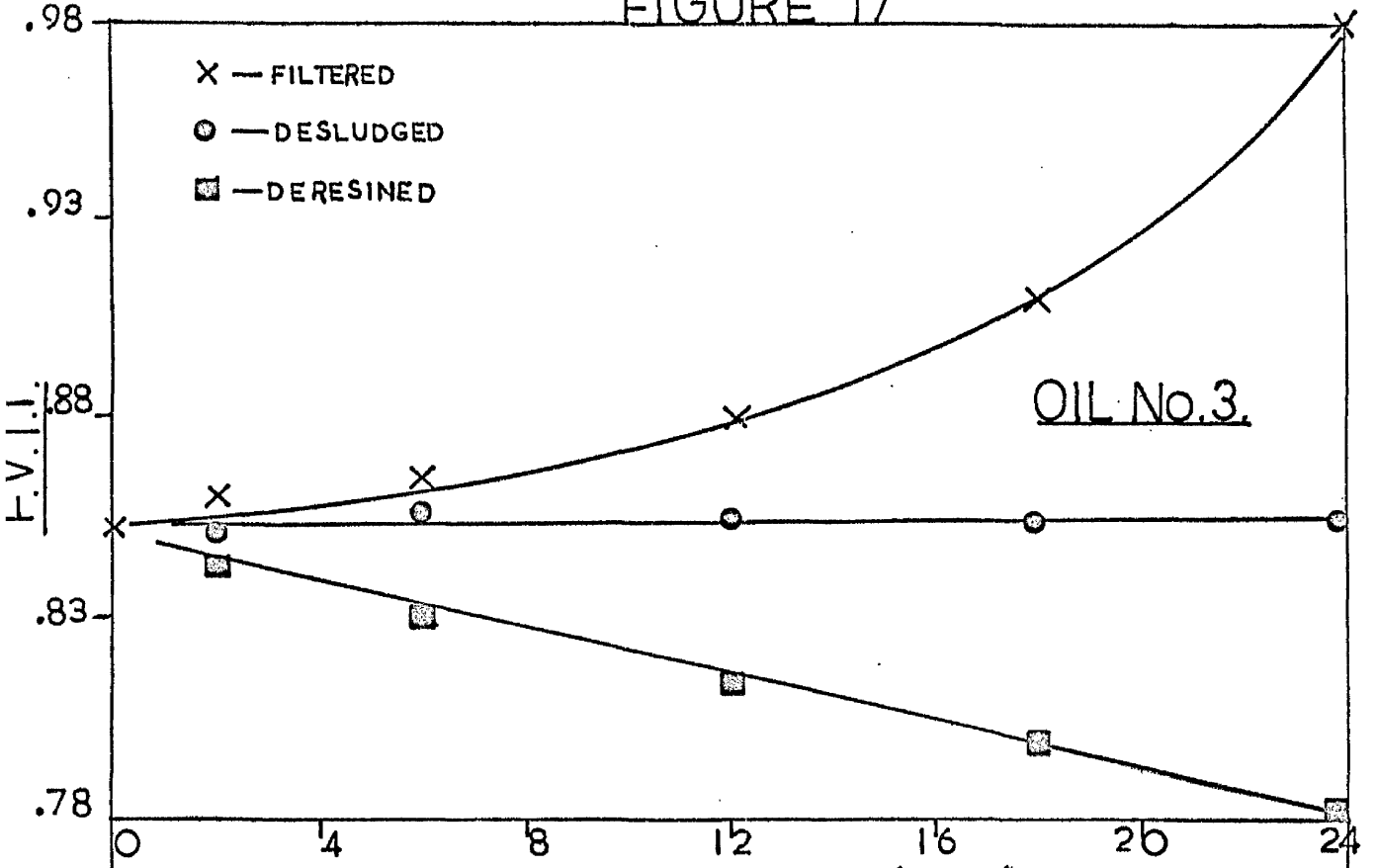
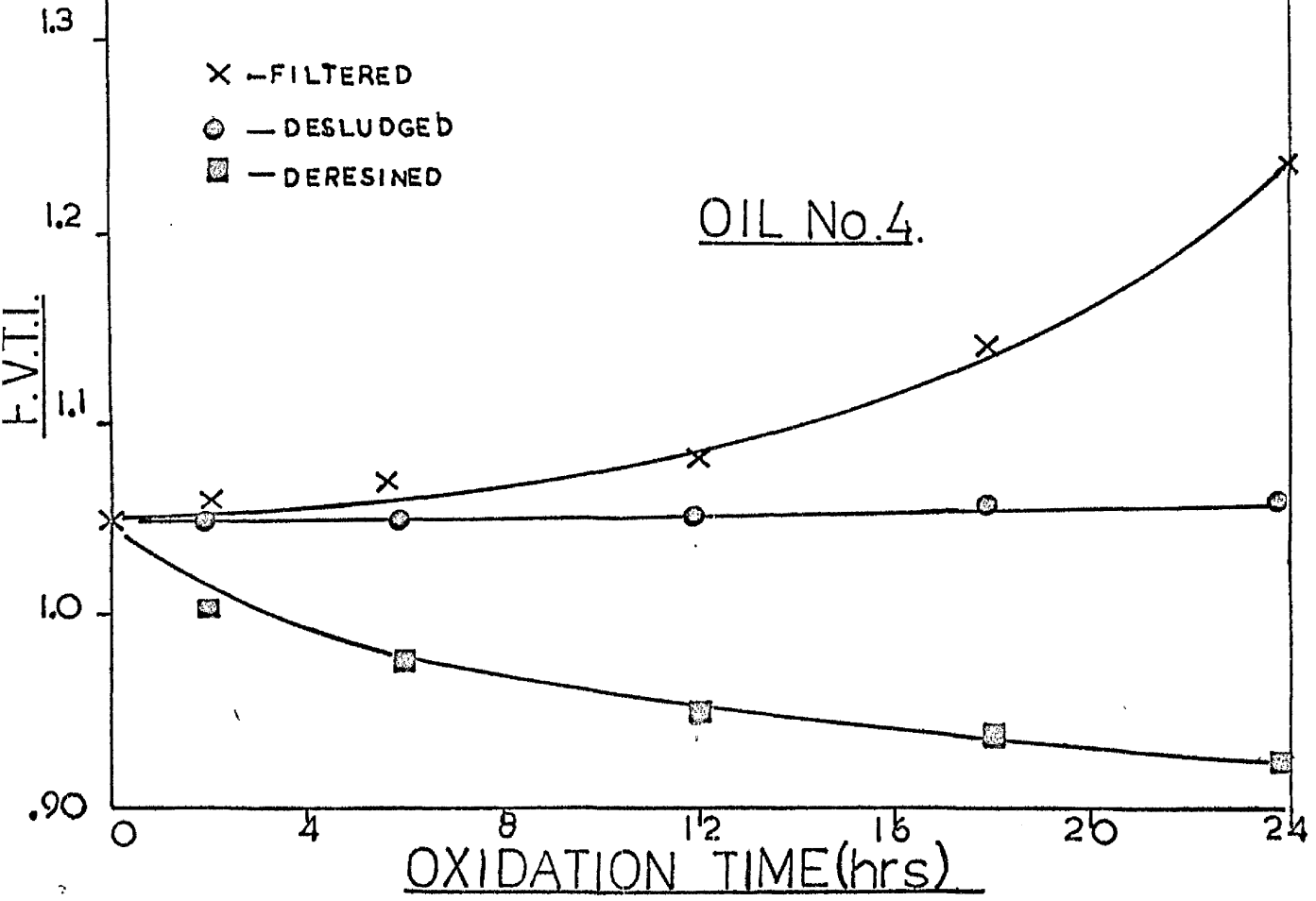

.80
.78
.76
.74
.72
F.V.I.I.
X — FILTERED
O — DESLUDGED
▣ — DERESINED
OIL No.1
0
4
8
12
16
20
24
OXIDATION TIME (hrs.)
.78
.76
.74
.72
.70
F.V.I.I.
X — FILTERED
▣ — DERESINED
OIL No.2
0
4
8
12
16
20
24
OXIDATION TIME (hrs)

FIGURE 17


× — FILTERED
⊙ — DESLUDGED
▣ — DERESINED
.98
.93
.88
.83
.78
F.V.I.I.
OIL No.3.
0
4
8
12
16
20
24
OXIDATION TIME (hrs)


× — FILTERED
⊙ — DESLUDGED
▣ — DERESINED
OIL No.4.
1.3
1.2
1.1
1.0
.90
F.V.T.I.
0
4
8
12
16
20
24
OXIDATION TIME (hrs)

The value of the Dean and Davis Viscosity Index is somewhat reduced by the fact that,

a) it is based on arbitrary standards;

b) it is not an additive property;

c) at very high range of V.I. the scale becomes meaningless;

d) anomalous results are obtained in the range of viscosities at 210°F. below 8c.s.

The F.V.T.I. put forward by Cornelissen and Waterman is claimed to be an absolute index and obviates the disadvantages of the Dean and Davis V.I. The relationship between viscosity and temperature is given by $\log V = (A/Tx) + B$

where V - viscosity in c.s.,

T - absolute temperature in degrees Kelvin,

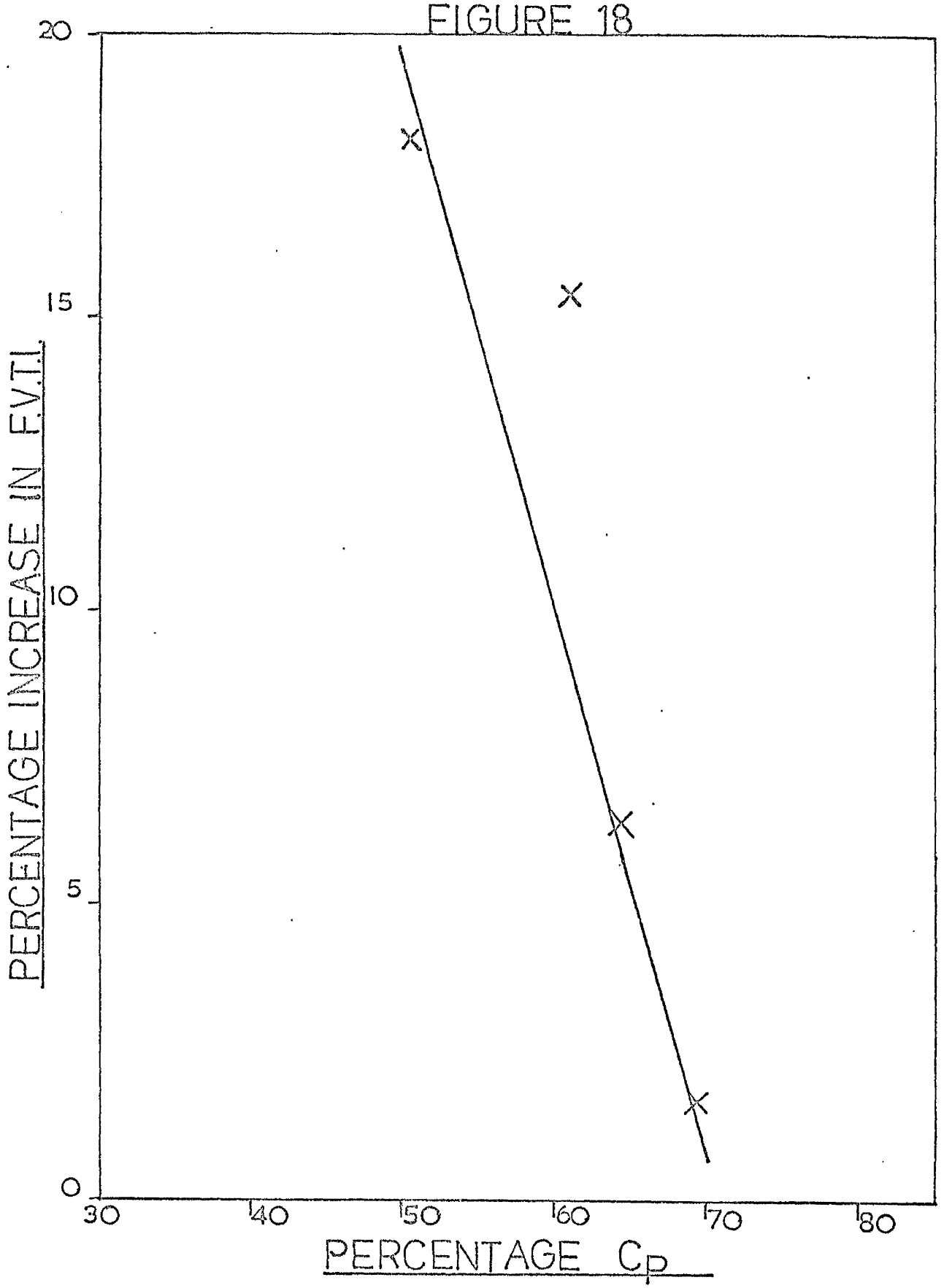
and A, B and x are constants.

All similar compounds have the same value for the constant "x".

In this investigation the F.V.T.I. was calculated by means of the relationship $\log (V_{20°C.}/V_{50°C.})$. From figure 15 the effect of oxidation on the F.V.T.I. of an oil can be seen. It would appear that the oils giving the greatest total viscosity increase also give the greatest change in F.V.T.I. For all oils the F.V.T.I. increases as oxidation progresses, in the case of Oils 3 and 4 at an ever increasing rate and in the case of Oils 1 and 2 at a linear rate.

The percentage increase in F.V.T.I. after 24 hours oxidation is in the order Oil 2 < Oil 1 < Oil 3 < Oil 4, which is the reverse of their order of oxidation stability. Oils with the greatest percentage of carbon

FIGURE 18


20
15
10
5
0
30
40
50
60
70
80
PERCENTAGE INCREASE IN F.V.T.L
PERCENTAGE C_p

in the paraffinic structure show the least change in F.V.T.I. and when the percentage increase in F.V.T.I. is plotted against percentage Cp a linear relationship can be observed (figure 18).

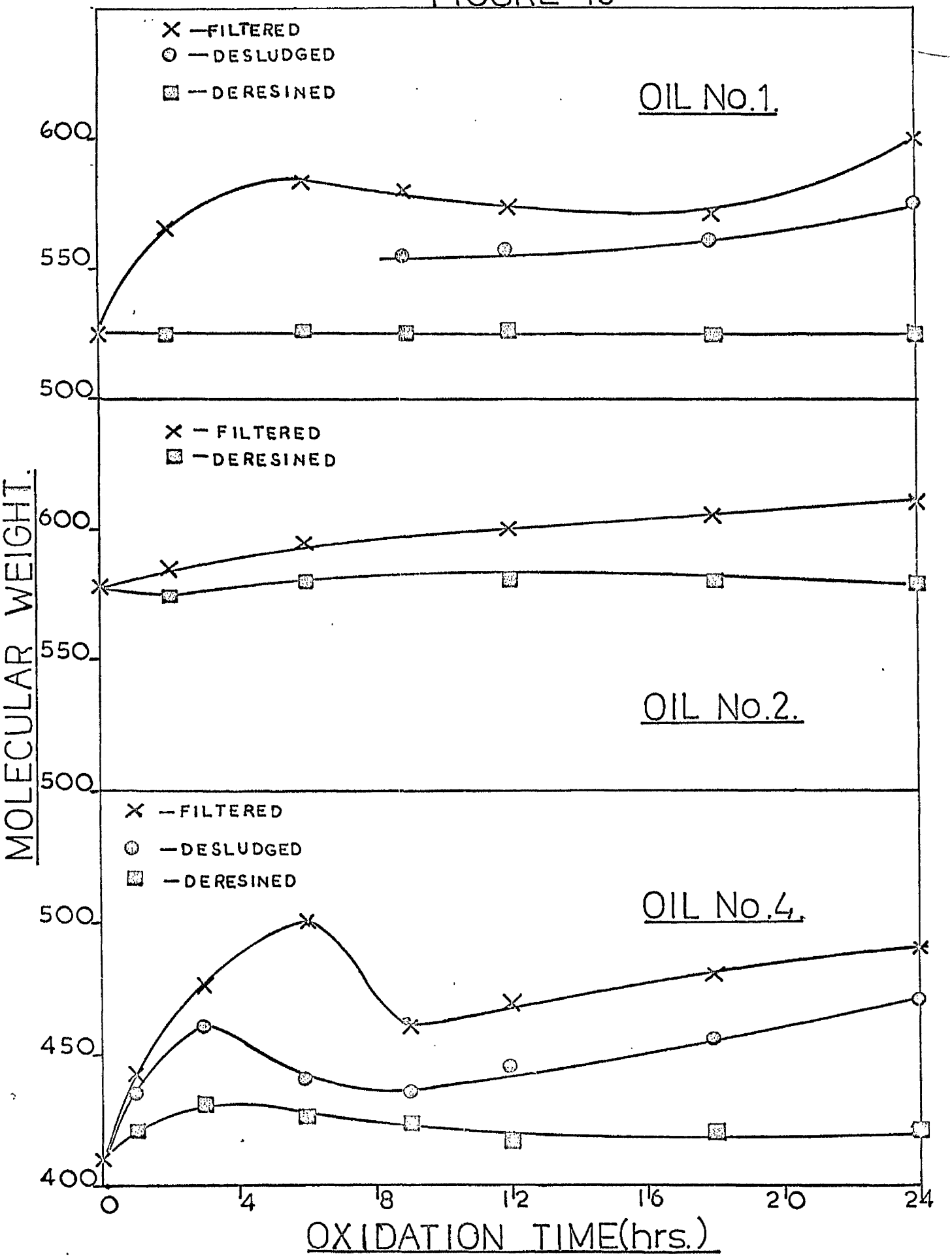
Figures 16 and 17 show the effect of removing sludge and resins from the oxidised oils. Removal of sludges reduced the F.V.T.I. to values only slightly above that of the original oil. When resins are removed, however, the F.V.T.I. was reduced to values lower than that of the original oil, the greatest reduction being in the oils which suffered the greatest attack during oxidation. This means that the materials formed as the result of oxidation have very poor temperature dependance properties, and when these are removed the recovered oils have a more desirable value of F.V.T.I. than the original oils.

Molecular Weight

The molecular weights were determined as described in the Appendix and the results expressed graphically in figure 19.

From this it can be seen that oxidation brings about an increase in the molecular weights of all three oils, the bulk of this increase occurring in the first stages of oxidation. In all three cases there is an initial rapid increase in the molecular weight, this increase being more pronounced in the case of Oil number 4 - the oil with the greatest aromaticity. The value for molecular weight reaches a maximum value after about 6 hours oxidation, followed by a slight decrease and then a final rapid increase. The sharp drop in molecular weight, after the initial maximum has been passes is more distinct in Oil number 4, but this oil does not show as great a final increase as does Oil number 1.

FIGURE 19


× —FILTERED
⊙ —DESLUDGED
▣ —DERESINED
OIL No.1.
600
550
500
× — FILTERED
▣ —DERESINED
600
550
OIL No.2.
500
× —FILTERED
⊙ —DESLUDGED
▣ —DERESINED
OIL No.4.
500
450
400
MOLECULAR WEIGHT.
0
4
8
12
16
20
24
OXIDATION TIME(hrs.)

The initial increase in molecular weight may be due to oxidation reactions producing heavier molecules, simply by addition of oxygen to the hydrocarbon molecules. Further oxidation may cause the formation of molecules which are more easily cracked at 200°C. and this may account for the sudden decrease in molecular weight in the range of 9 hours oxidation. After this time polymerisation reactions may be more predominant and hence bring about the final increase in molecular weight.

When sludges are removed there is a drop in molecular weight but the average molecular weight of the desludged oil is still greater than that of the original oil. Oil number 4 once again shows the greatest change. It would appear then that the molecular weight of sludge itself must be considerably greater than the molecular weight of the oil.

When the molecular weights of the deresined oils were determined it was found that the recovered samples from Oils 1 and 2 had molecular weights in the same range as the original oils, and that those from Oil number 4 had slightly greater molecular weights than the original oil. This would indicate that Oils 1 and 2 are composed of hydrocarbons of similar molecular weight. In the case of Oil number 4 the initial attack appeared to be on the lighter hydrocarbons so that the molecular weight of the deresined oil increased. This indicated a greater diversity of hydrocarbon type present in Oil number 4 which was also the least refined of the oils. After the initial increase in the molecular weight of Oil number 4 there was a very slight decrease followed by more constant values up to 24 hours oxidation.

CHAPTER VIII

CHAPTER VIII

NATURE OF THE OXIDATION PRODUCTS AND OF THE OILS RECOVERED BY FULLERS EARTH TREATMENT

1. Properties of the oxidation products

Examination of sludges and resins requires that they be separated from the oxidised oil. For accurate analysis, it is necessary that they undergo no change during separation. Since resins apparently suffer no change during separation from the oxidised oil, e.g. they re-dissolve in the oil, it is possible to examine them directly but since the means of separating sludge involves peptisation and aggregation, it is not satisfactory to examine its properties directly. Davis et al (90) also found that resins could re-dissolve in the oil, but that sludges could not re-dissolve.

The difficulty in examining sludge and resins was overcome by determining the properties of the oil before and after sludge and resin removal and, with a knowledge of the weights of sludge and resins present, it was possible to determine their properties. The properties of a few samples of sludge and resin were found directly and compared with the calculated values. It was found that sludge showed great differences in values whereas those for the resins compared favourably.

Density

The density of an oxidised oil sample can be expressed by the equation:

$$dav = \frac{w_1 + w_2}{\frac{w_1}{d_1} + \frac{w_2}{d_2}}$$

where d = density of the desludged oil;

w_1 = weight of the desludged oil;

d_2 = density of sludge

and w_2 = weight of sludge present.

It is possible to express the density in this manner since the oxidised oil is a homogeneous mixture of similar substances. Hence, the density of sludge may be expressed as:

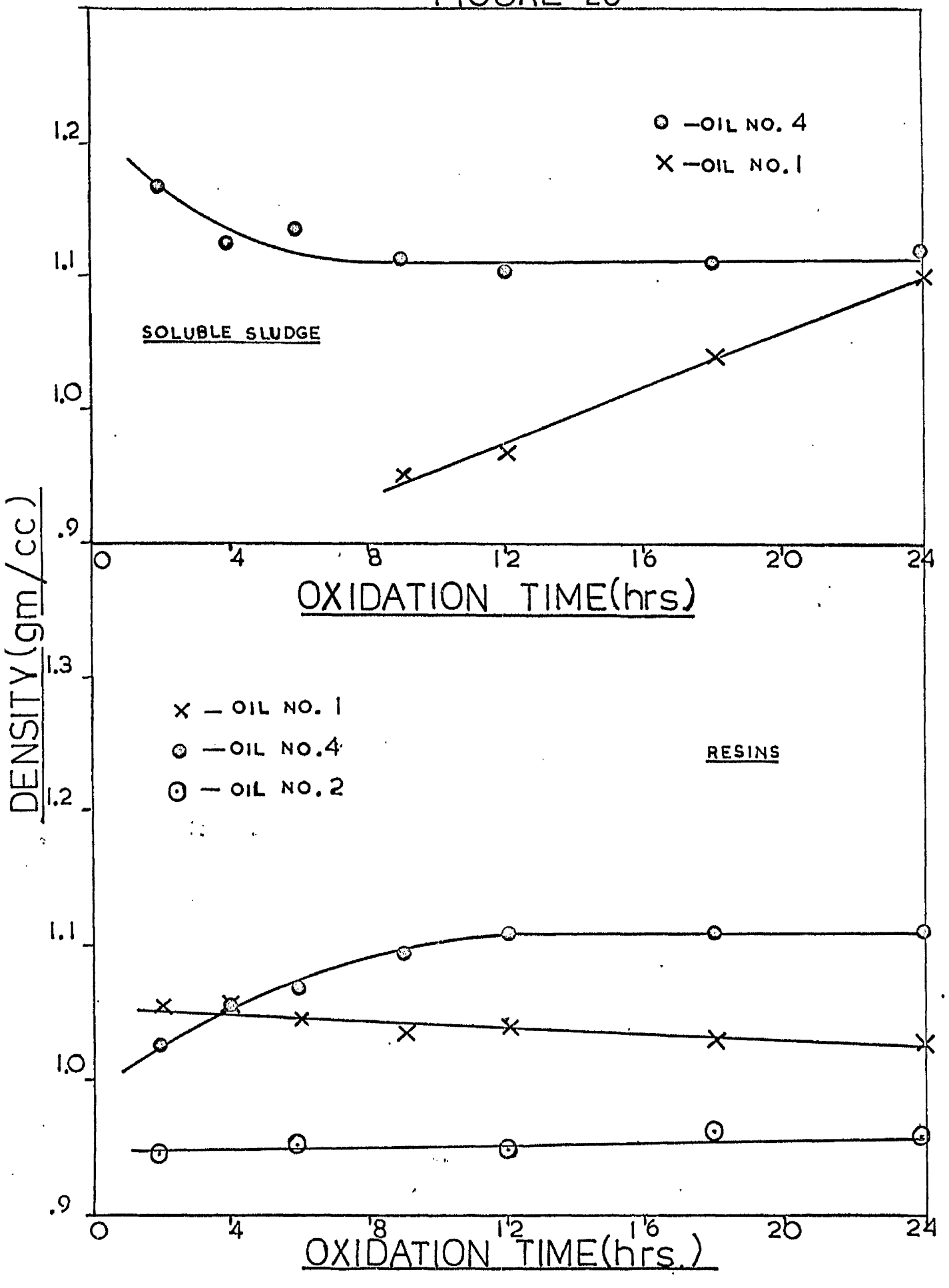
$$d_2 = \frac{(dav \cdot w_2 \cdot d_1)}{(w_1 + w_2)\, d_2 - (dav \cdot w_1)}$$

Similarly the density of resins may be calculated.

From figure 20 it is obvious that the densities of both resins and sludge are greater than those of the original oils. The sludge formed by Oil number 1 shows a continuous increase in value, whereas that of Oil number 4 shows an initial decrease up to 12 hours oxidation and then tends to a constant value. This indicates that equilibrium had been reached in the case of Oil number 4 and had not yet done so in the case of Oil number 1.

The resins formed in Oil number 4 showed an initial increase in density, where the sludge showed a decrease. After about 12 hours oxidation the densities of the resins tended towards a constant value asdid the sludge. The resins formed by all three oils showed a tendency towards constant values indicating that the resins formed were of a uniform nature. If resins are to be considered as intermediate products in the formation of sludge, the tendency towards constant values must be expected.

FIGURE 20


DENSITY (gm/cc)
1.2
1.1
1.0
.9
O —OIL NO. 4
X —OIL NO. 1
SOLUBLE SLUDGE
0
4
8
12
16
20
24
OXIDATION TIME(hrs)
1.3
1.2
1.1
1.0
.9
X — OIL NO. 1
O —OIL NO. 4
O — OIL NO. 2
RESINS
0
4
8
12
16
20
24
OXIDATION TIME(hrs.)

Molecular Weight

An approximate value for the molecular weight of a homogeneous mixture of two similar compounds can be calculated using the equation:

$$Mav. = (x_1 . M_1) + (x_1 . M_2)$$

where M_1 and M_2 are the molecular weights of the two compounds, and x_1 and x_2 the weight fractions of the two components.

If Mav. is the molecular weight of an oxidised oil sample, x_1 the weight fraction of the desludged oil present, and M_1 the molecular weight of the desludged oil, then M_2 the molecular weight of the sludge can be calculated from:

$$M_2 = (Mav - x_1M_1)/x_2$$

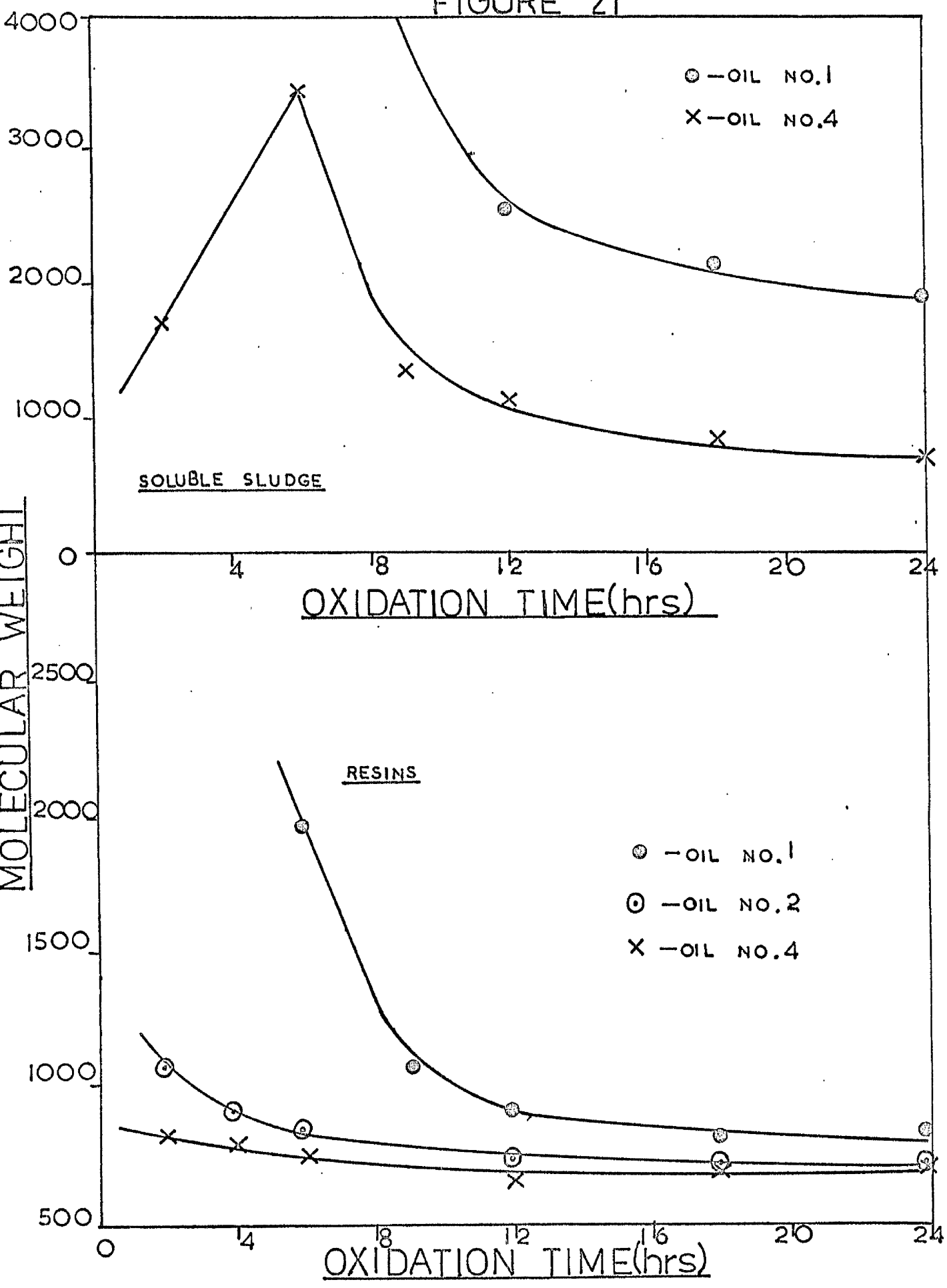
where x_2 = weight fraction of the sludge.

Similarly the molecular weight of resins can be calculated.

The molecular weights of the resins formed by all three oils tended towards a constant value (figure 21) after very high initial values. The resins from all three oils tended to have values a little greater than those of the original oils, which agrees with the work done by Sachanen and Vassilieff (100) and Haus (101) who found that resins derived from lubricating oil distillates all had values comparitively close to that of the original oil.

Soluble sludge molecular weights were initially greater than those of the resins (figure 21), but in the later stages of oxidation tended towards values similar to that of the resins. After an initially very high value the

FIGURE 21


4000
3000
2000
1000
0
⊙ — OIL NO.1
× — OIL NO.4
SOLUBLE SLUDGE
4
8
12
16
20
24
OXIDATION TIME(hrs)
MOLECULAR WEIGHT
2500
2000
1500
1000
500
RESINS
⊙ — OIL NO.1
⊙ — OIL NO.2
× — OIL NO.4
0
4
8
12
16
20
24
OXIDATION TIME(hrs)

molecular weight of sludge from Oil number 1 decreased and was still decreasing after 24 hours but yet had to reach the same value as the sludge from Oil number 4. Sludge from Oil number 4 tended towards a molecular weight which seemed to indicate that dimerisation had taken place.

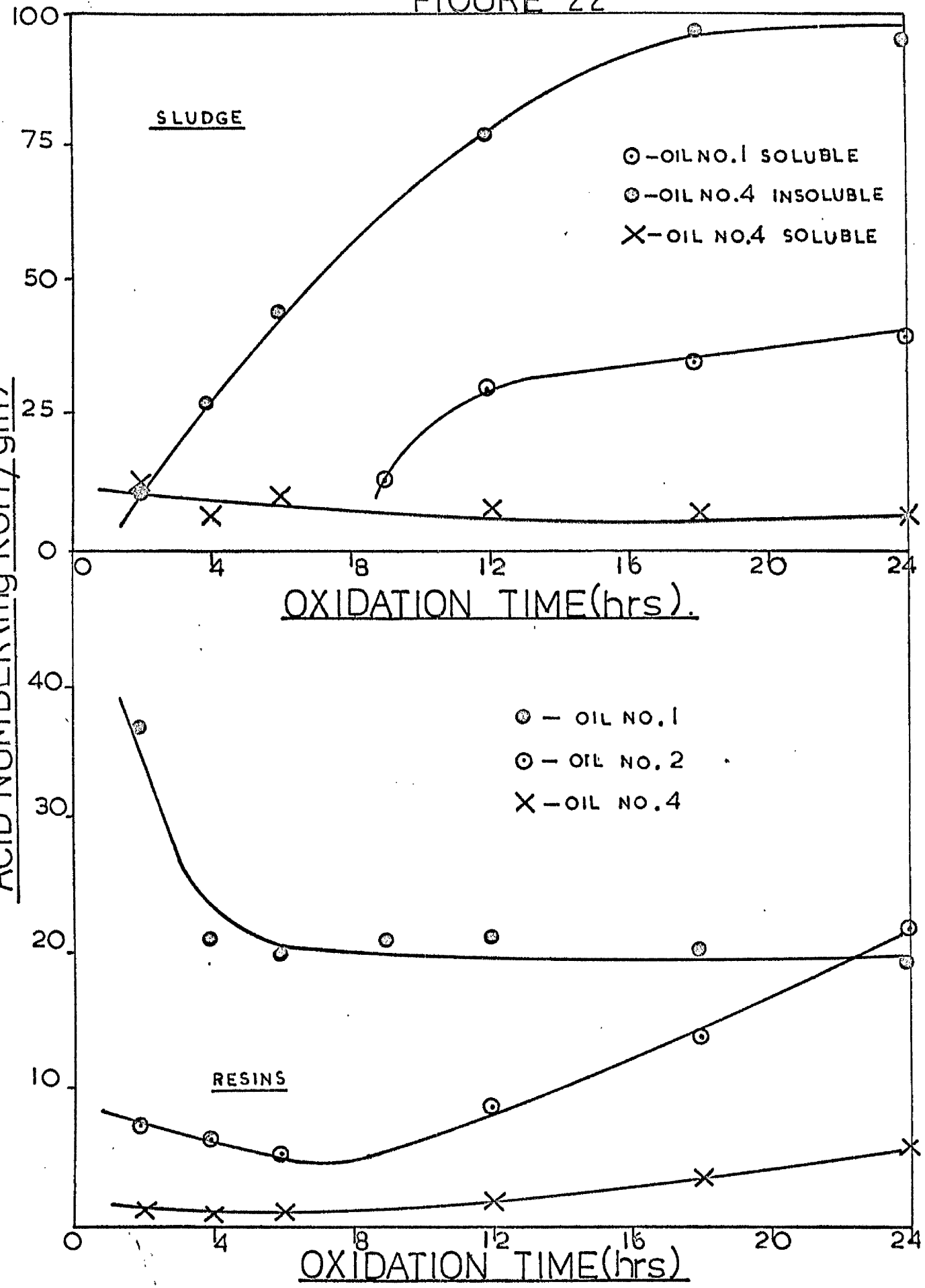
Molecular weights of soluble sludge obtained in this investigation are comparable with those obtained by Fenske et al (65) by a cryoscopic method, and by Sachanen (102) by an ebullioscopic method. Values have also been obtained by other works (103,104,105), using a variety of techniques, which differ greatly from those obtained in the present work. Values obtained ranged from 9,000 to 140,000, but such earlier molecular weight determinations were carried out on sludge separated from the oxidised oil and the wide variation in values obtained might have been due to differences in degree of aggregation during precipitation of the sludge.

Acid Number

The acid numbers of soluble sludge and resins formed by Oil number 4 are both in the same range, but the acidity of the insoluble sludge formed by this oil was much greater. Figure 22 also shows that Oil number 1 formed soluble sludge which, unlike that of Oil number 4, was more acidic than the corresponding resins. The acid number of the resins from Oil number 2 was intermediate between those from Oils number 1 and 4, although after 24 hours it was greater than that of Oil number 1 and still increasing.

That the oils containing the greatest amount of paraffinic carbon were also the oils which tended to produce the more acidic resins, was no doubt due to the fact that paraffins on oxidation usually produce more acids than do other types of hydrocarbons.

FIGURE 22


SLUDGE
⊙-OIL NO.1 SOLUBLE
⊙-OIL NO.4 INSOLUBLE
×-OIL NO.4 SOLUBLE
100
75
50
25
0
0
4
8
12
16
20
24
OXIDATION TIME(hrs).
ACID NUMBER mg KOH/gm
40
30
20
10
⊙ — OIL NO.1
⊙ — OIL NO.2
× — OIL NO.4
RESINS
0
4
8
12
16
20
24
OXIDATION TIME(hrs)

Considerably less sludge was formed by these oils and hence less acidic material could be transferred from resins to soluble sludge. Also, where sludge was formed, the resins tended to have a more constant acid value - unlike the resins from Oil number 2.

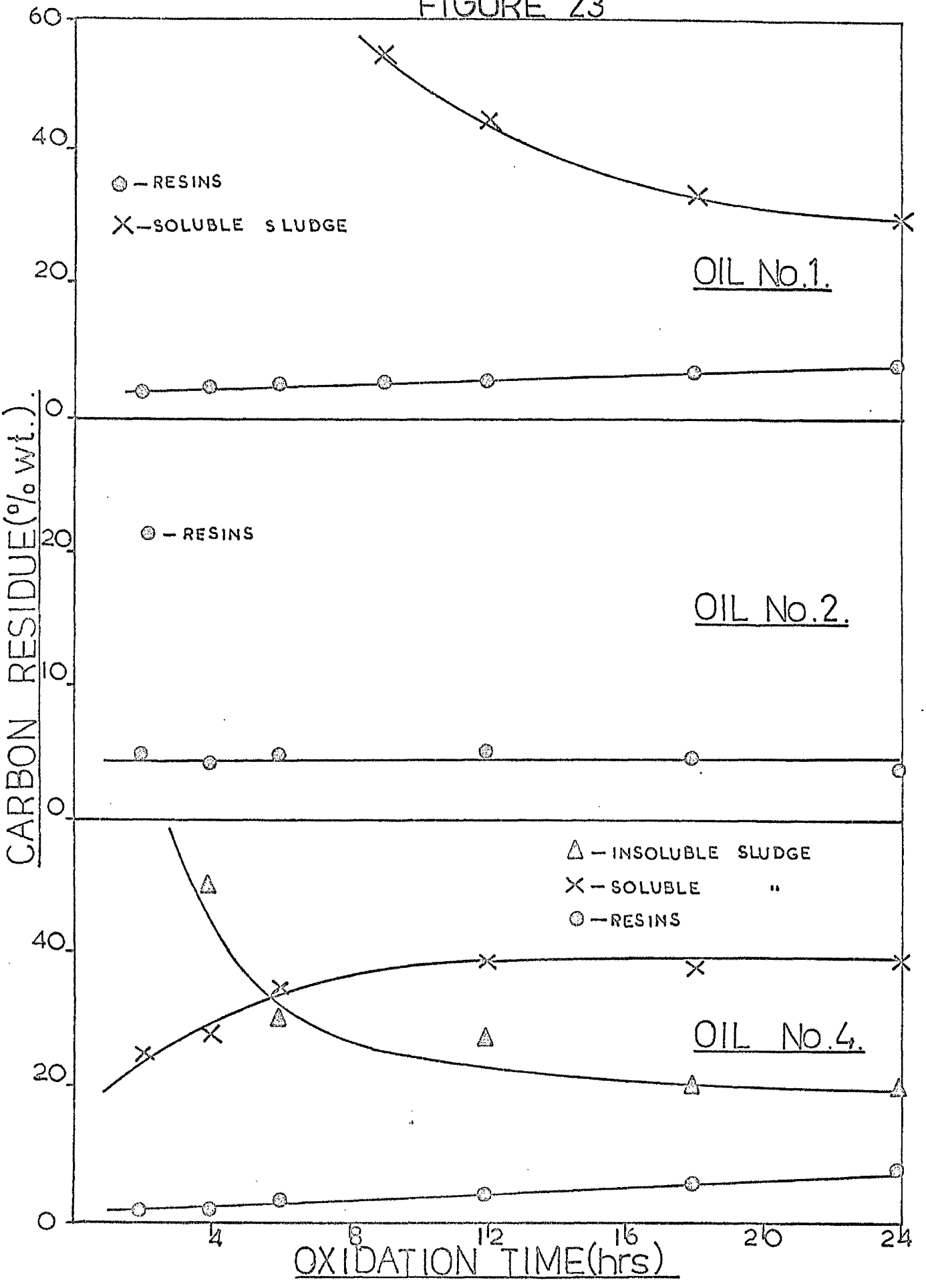
Where insoluble sludge had been formed (Oil number 4) the acid number of the soluble sludge tended towards a constant value, and in the case of Oil number 1, which formed soluble sludge only, the acidity continued to increase even after 24 hours oxidation.

Carbon Residue

Sludges and resins have a much greater carbon residue than the original oil (figure 23), but resins have a relatively smaller carbon residue than either insoluble or soluble sludge. Where sludge was formed, Oils 1 and 4, the carbon residue of the resins tended to increase slightly with oxidation time, but where no sludge formed the carbon residue of the resins remained constant (Oil number 2).

The soluble sudge formed by Oil number 1 after 9 hours oxidation showed a decreasing carbon residue as oxidation progressed, but tended towards a constant value in the same range as that of the soluble sludge formed by Oil number 4. The insoluble and soluble sludges formed by Oil number 4 both tended towards constant carbon residues with soluble sludge having the greater value. In the first stages of oxidation, however, insoluble sludge had the greatest carbon residue, but after about 6 hours oxidation the soluble sludge carbon residue had increased sufficiently to become the highest value.

FIGURE 23


60
40
20
0
RESINS
SOLUBLE SLUDGE
OIL No.1.
20
0
RESINS
OIL No.2.
10
0
INSOLUBLE SLUDGE
SOLUBLE "
RESINS
40
20
OIL No.4.
0
4
8
12
16
20
24
CARBON RESIDUE(% wt.).
OXIDATION TIME(hrs)

The fact that the carbon residues of the resins were all comparatively low indicated that they were not polymerised to any great extent, unlike the sludges which appeared to be polymerised - with soluble sludge more so than the insoluble sludge. This may have been caused by the further oxidation of soluble sludge to insoluble sludge giving oxidation products which were more easily cracked under the conditions of the Ramsbottom carbon residue determination.

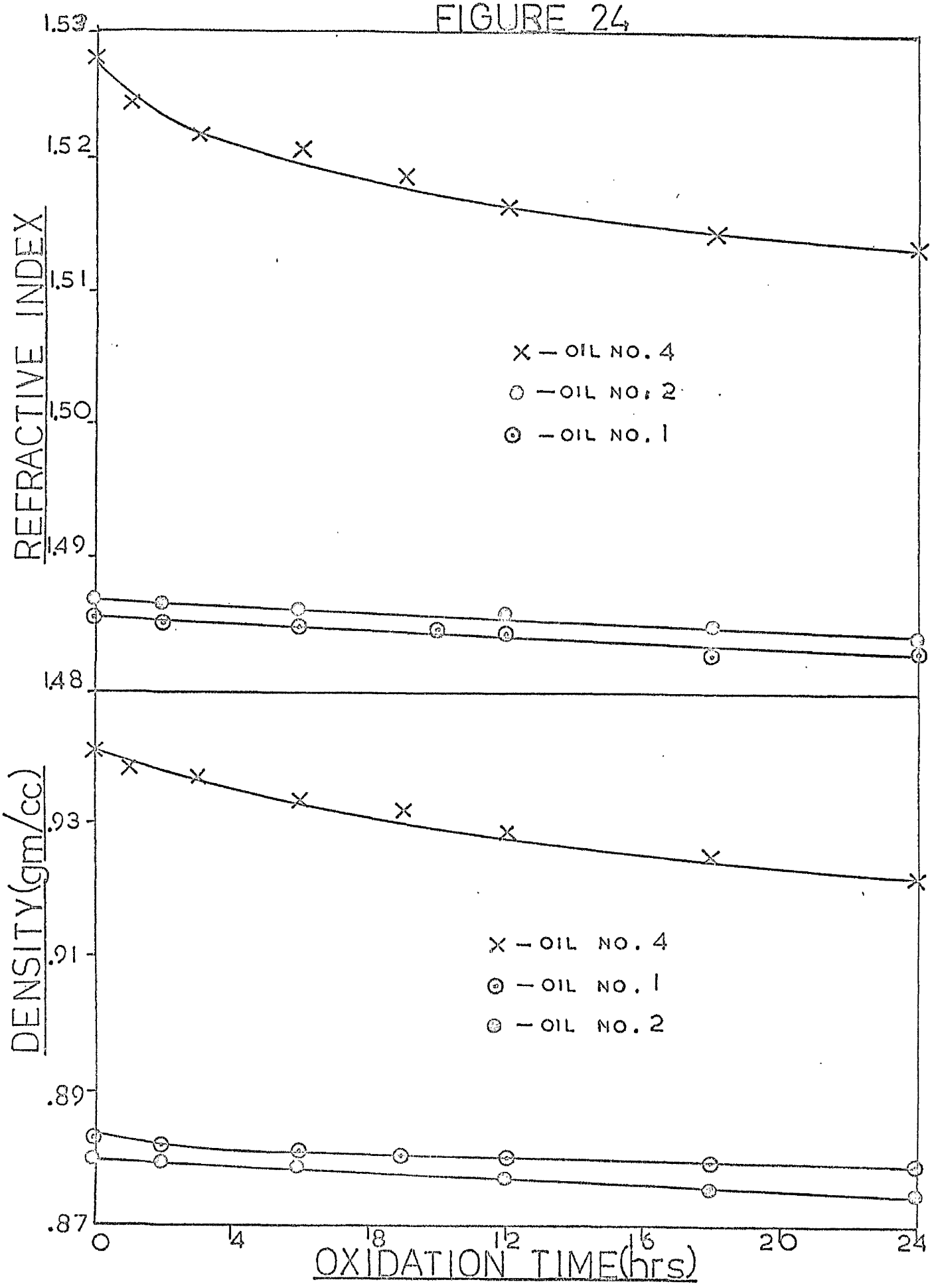
2. Properties of the recovered oils

Davis, Lincoln, Byrkit and Jones (90) removed resins stepwise from an oxidised oil and found that the oxygen content, carbon residue, neutralisation number and saponification number all approximated those of the original oil. This tendency for deresined oils to approach the characteristics of the original oil was apparent in the present investigation and was also observed by Poell (106), Noack (107), Suida (108), Marcusson (109) and Schindler (110).

The oil recovered after Fuller's earth treatment was that part of the original oil which had not undergone oxidation. All the deresined samples obtained in the present work were similar in colour to the original oils but had lost their characteristic aromatic "bloom".

The refractive indices of the recovered oils are shown graphically in figure 24, and from this it can be seen that in all three cases the refractive index decreases with oxidation time. Oils 1 and 2 show a linear decrease in the refractive indices of the recovered oils, but in the case of Oil number 4 the decrease is rapid at first and then almost linear after about 4 hours oxidation.

FIGURE 24


1.53
1.52
1.51
1.50
1.49
1.48
REFRACTIVE INDEX
X — OIL NO. 4
O — OIL NO. 2
⊙ — OIL NO. 1
.93
.91
.89
.87
DENSITY (gm/cc)
X — OIL NO. 4
⊙ — OIL NO. 1
⊙ — OIL NO. 2
0
4
8
12
16
20
24
OXIDATION TIME (hrs)

A decrease in density of the deresined oils was apparent, the graphs of density against oxidation time being similar to those of the refractive index. Once again Oil number 4 shows the greatest change followed by Oil number 2 and then Oil number 1.

For Oil number 1 the molecular weights of the recovered oils are in the same range as that of the original oil. Oils 2 and 4 however show an increase in molecular weight - only a slight increase in the case of Oil number 2 but much greater in case of Oil number 4. The variation in molecular weight can be clearly seen in figure 19, Oil number 4 showing greater variation in molecular weight than did Oils 1 and 2.

Acid numbers of the recovered oils from all three original oils were either the same as, or slightly greater than, those of the original oil samples but very much lower than the acid numbers of the oxidised oils.

The deresined oils all had viscosities at 20°C. which were lower than those of the original oils and tended to decrease with oxidation time. Oil number 4 again showed the greatest decrease followed by Oil number 2 and then Oil number 1. The F.V.T.I. of the recovered oil samples were lower than that of the original oil, showing that the viscosities of the recovered oils are less temperature dependant.

From the foregoing observations it was apparent that the material which suffered attack during oxidation is that which contributed most to the viscosity, density and refractive index of the original oils. It was also apparent that the hydrocarbons which made up Oils 1 and 2 were of a more uniform nature than those of Oil number 4, since Oils 1 and 2 showed the least amount of change from the original oils when they were deresined.

3. Structure of the recovered oils

After removal of oxygenated compounds by means of Fuller's earth the recovered, or deresined, oils were capable of being examined by means of the Waterman Ring Analysis (29). By this means the distribution of carbon among the paraffinic, naphthenic and aromatic portions of the deresined oils, and the number of different ring structures in the mean molecule, were determined. The results of this analysis are shown in figures 25,26 and 27.

The deresined oils from Oil number 1 showed very little change in the percentage C_p, any change being a slight increase. The percentage C_N showed an overall increase after 24 hours, but up to 9 hours oxidation there was a slight decrease which was followed by a slightly greater increase. A decrease in the percentage C_A was observed up to 9 hours, and after this time the rate of decrease became faster. Similar tendencies were shown in the ring distribution in the mean molecule. R_T showed a linear rate of decrease, R_N showed a decrease up to 9 hours oxidation and then increased, and the rate of decrease in R_A increases after 9 hours. From this it would appear that both aromatic and naphthenic components are concerned in resin formation and that aromatics are more important in the formation of sludge.

Only the percentage C_N and C_p of the de-resined oils from Oil number 2 show any change (figure 26), the percentage C_N decreased while the percentage C_p increased slightly. The percentage aromatic content showed no change from that of the original oil. R_N also decreases with oxidation time, and since R_A remains constant the total number of rings per mean molecule also decreases. Once again it would appear that the naphthenic portion of the oil is mainly concerned with resin production since Oil number 2 formed resins only.

FIGURE 25

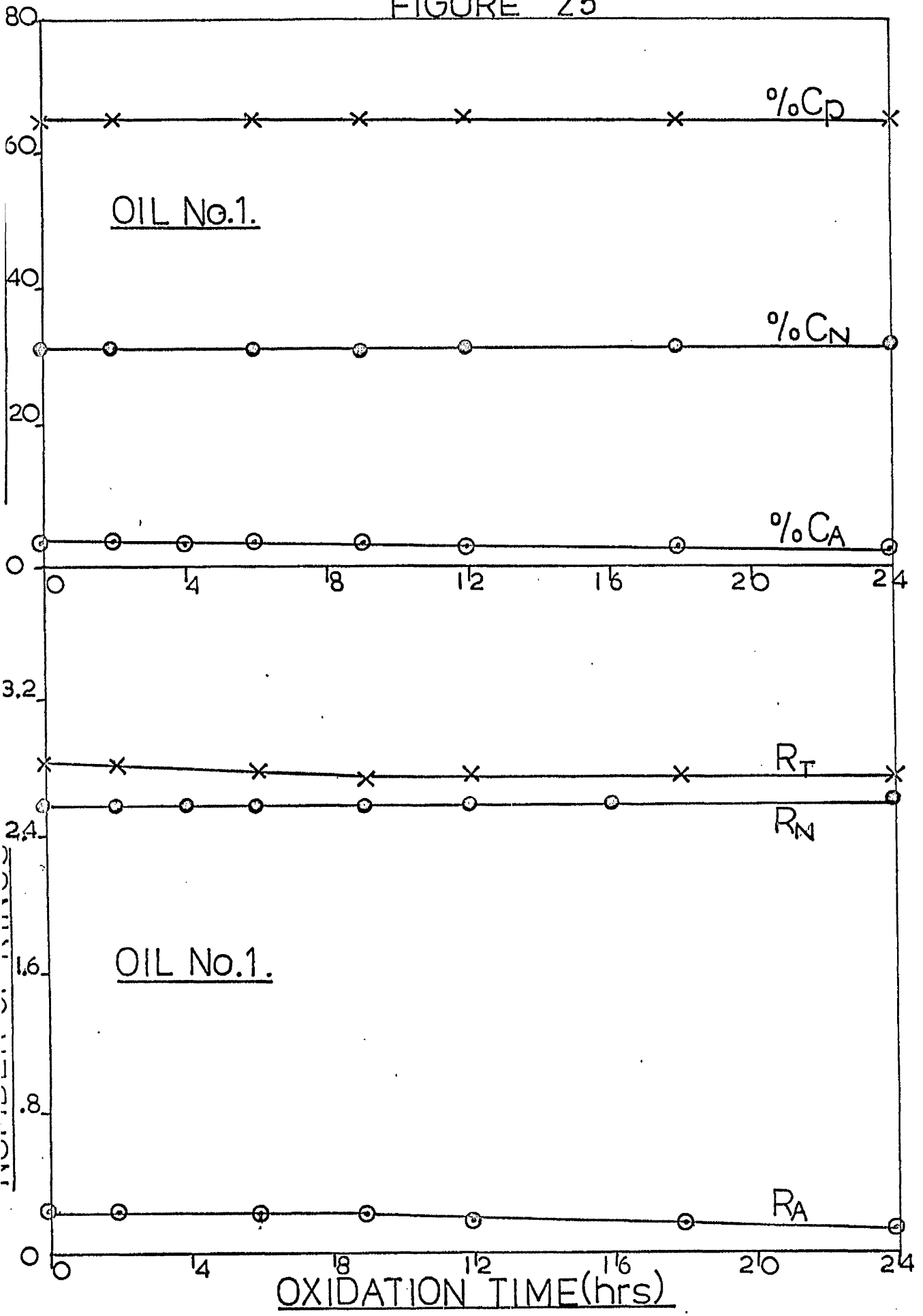

80
60
40
20
0
%Cp
%CN
%CA
OIL No.1.
0
4
8
12
16
20
24
3.2
2.4
1.6
.8
0
RT
RN
RA
OIL No.1.
0
4
8
12
16
20
24
OXIDATION TIME(hrs)

FIGURE 26

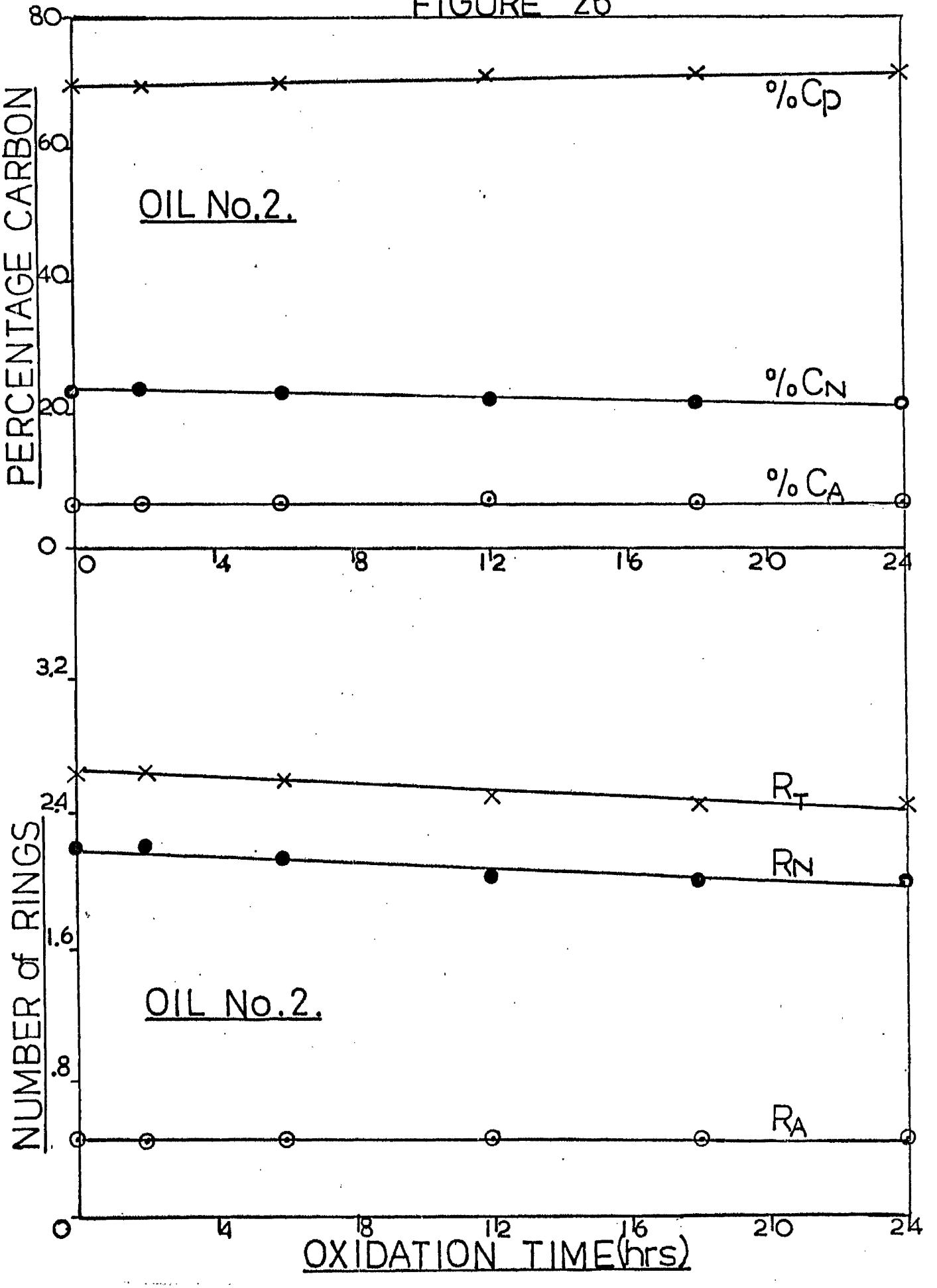
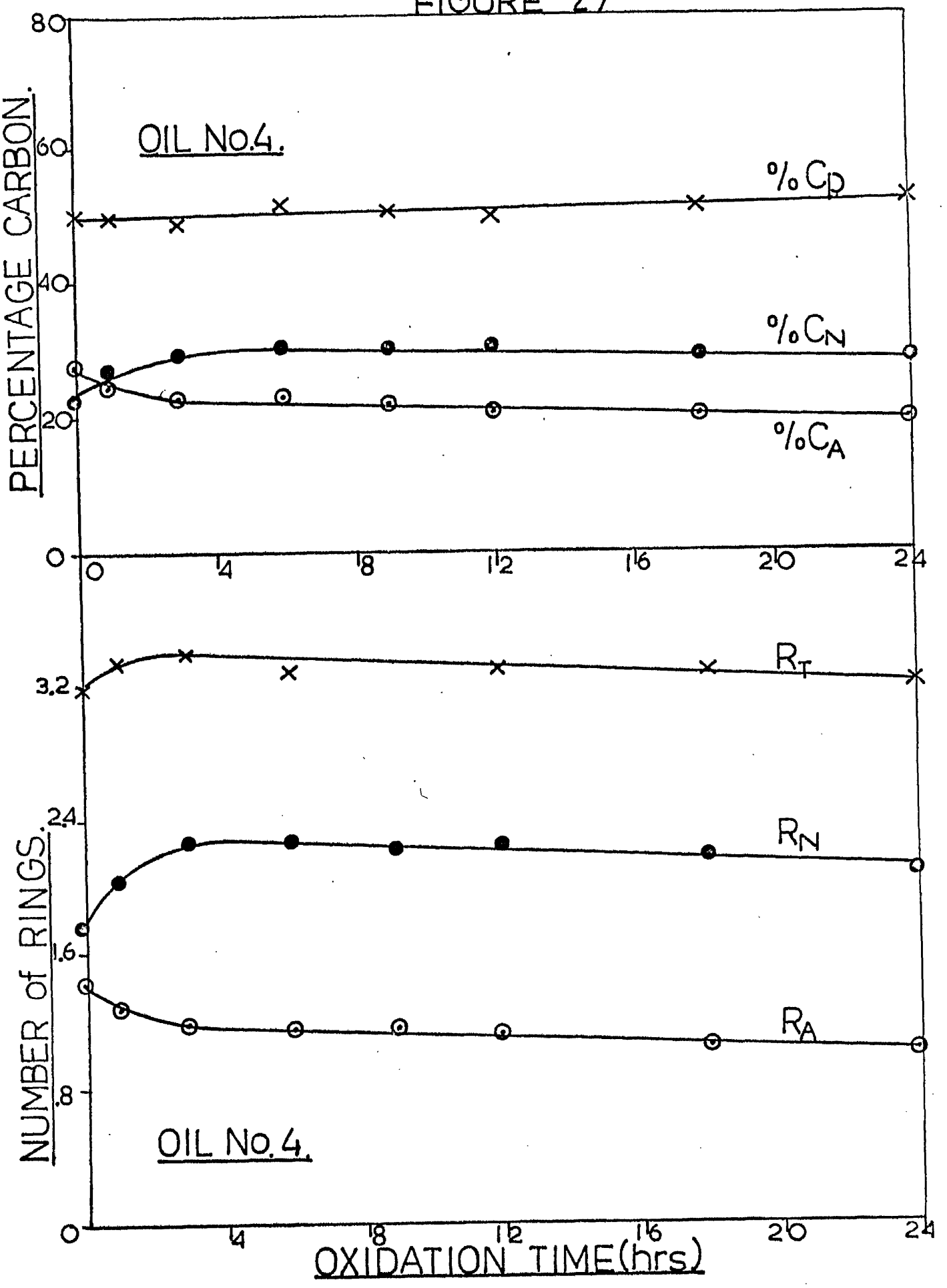

PERCENTAGE CARBON
80
60
40
20
0
%Cp
%CN
%CA
OIL No.2.
0
4
8
12
16
20
24
NUMBER of RINGS
3.2
2.4
1.6
.8
0
RT
RN
RA
OIL No.2.
OXIDATION TIME(hrs)

FIGURE 27


OIL No.4.
PERCENTAGE CARBON.
80
60
40
20
0
%C_D
%C_N
%C_A
0
4
8
12
16
20
24
3.2
2.4
1.6
.8
R_T
R_N
R_A
NUMBER of RINGS.
OIL No.4.
OXIDATION TIME(hrs)

When Oil number 4 was examined in this manner (figure 27) a much greater variation in values is observed. As before, the percentage C_P showed little change after 24 hours oxidation and in fact increases slightly. The percentage C_A and the number of aromatic rings per molecule show a rapid decrease up to 3 hours, the rate of decrease after this time being linear. Up until 3 hours the percentage C_N and the number of naphthenic rings per mean molecule increase rapidly and then decreased at a uniform rate, but were still greater in value after 24 hours than the original oil. The initial decrease in aromatic content was association with an increase in molecular weight which indicates that low molecular weight aromatics suffer the first oxidative attack. After 3 hours the percentage C_A and C_N, and the number of aromatic and naphthenic rings decreased at the same rate - indicating that they were being oxidised simultaneously.

CHAPTER IX

PART II

RELATION BETWEEN OXIDATION AND VISCOSITY

Many workers have estimated the oxidation stability of lubricating oils and pure hydrocarbons by their ability to absorb oxygen. High absorption of oxygen does not necessarily mean that the oil has a low oxidation stability. What is more important is the amount and nature of oxidation products formed, and their effect upon the properties of the oil.

It has been shown that highly refined oils absorb the greatest amount of oxygen (67), but that highly refined oils also produce the smallest amount of retained oxidation products. Thus with highly refined oils the bulk of oxidation is apparently concerned with the production of volatile materials. It should be expected that two more refined oils produce resins and volatile products, while two less refined oils produce resins, sludge and volatile products. In this respect highly refined oils are taken to be those containing fewer aromatics since refining tends to remove aromatics.

It has also been found by several workers (4,5,111,62) that the absorption of oxygen passed through a mineral oil at 10° centigrade, but that the amount of total sludge formed increased with increasing aromatic content, and that the proportion of volatile sludge decreased as the percentage aromatics increased. Other workers (110,112) have also reported that the total sludge formed during the course of oxidation was a function of the percentage aromatics in the original lubricant.

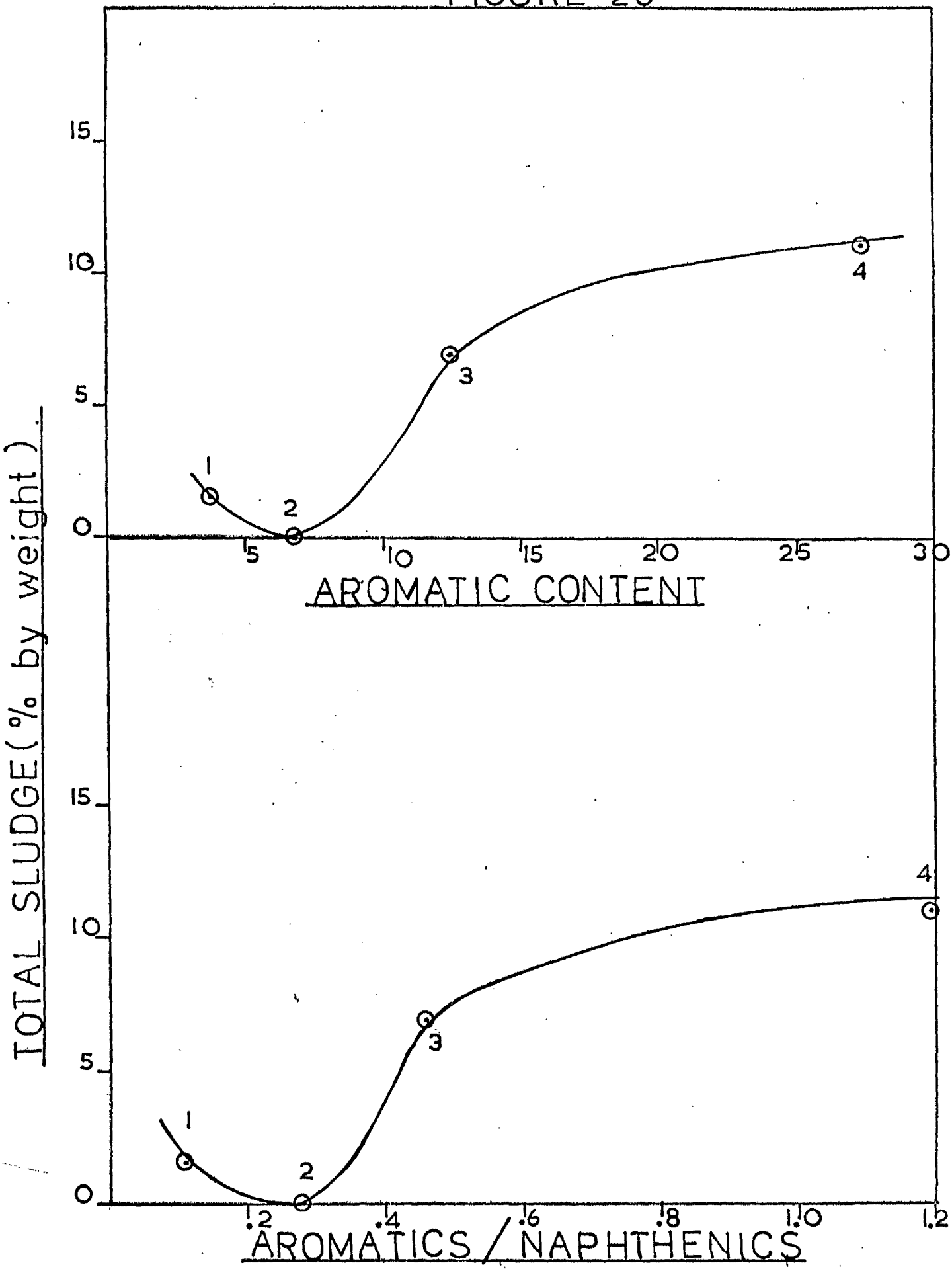
In the present work it was found that the formation of sludge depended upon whether or not the original oil contained more, or less, than 6-8% aromatics. Oil number 2 with 6.7% aromatics produced no sludge, whereas Oil number 1 (3.8% C_A) produced soluble sludge and Oil number 4 produced both soluble and insoluble sludge. Thus it would appear that, under these particular oxidation conditions, there was an optimum aromaticity for the production of sludge. This can be substantiated if the values obtained by Beaton (88) are included in the graph of total sludge formed against oxidation time (figure 28). A similar effect was also found by Fenske (65). This effect may be an explanation of the "optimum aromaticity" with respect to oxygen absorption, since resins have a lower oxygen content than sludge (88,67). Also, oils which give resins rather than sludge tend to give greater amounts of volatile products and hence retain a smaller amount of oxygen.

From the evidence obtained in the present work it would appear that the aromatics were concerned with the formation of sludge, while the naphthenic materials were concerned with resin formation.

Whether an oil formed sludge or not was dependant upon the ratio of aromatic to naphthenic content, a similar optimum effect being observed as that of aromaticity. This is clearly seen in figure 28 where $C_A:C_N$ was plotted against total sludge formed. Oil number 2 ($C_A:C_N=0.27$) formed no sludge and the deresined oils show a decrease in percentage naphthenic materials with oxidation time, indicating that the naphthenic material present may have been forming oxidation inhibitors which hindered the oxidation of aromatics to sludge.

The carbon residues of the oxidised oils have been found to increase with their aromatic contents by other workers, but this was not so in this work.

FIGURE 28


TOTAL SLUDGE (% by weight)
15
10
5
0
1
2
3
4
5
10
15
20
25
30
AROMATIC CONTENT
15
10
5
0
1
2
3
4
.2
.4
.6
.8
1.0
1.2
AROMATICS / NAPHTHENICS

Whether an oil has a greater or lesser increase in carbon residue than another depends upon the amount and type of sludge produced upon oxidation. Figure 7 shows that the oils which produced sludge had a greater increase in carbon residue than the oil which produced only resins, and that the oil which also formed insoluble sludge had the greatest increase of all.

Viscosity increase during oxidation showed no dependance upon the aromaticity of the original oils. The increase in viscosity did depend upon whether or not sludge was produced. The oils which produced sludge showed the greatest increase in viscosity, the actual increase being directly proportional to the amount of sludge formed. Insoluble sludge formed by Oil number 4 had been filtered off, and hence the increase in viscosity shown in figures 12 and 13 was not a true value, the viscosity increase being greater than that shown. Resins contributed more to the viscosity increase than the sludge in the initial stages, but eventually the contribution of the soluble sludge was greater since sludge had a greater viscosity than resins.

The increase in total acidity of the oxidised oils was apparently dependant upon the amount of total oxidation products formed, which showed some dependance upon the aromaticity of the oils. Removal of sludge reduced the acid numbers considerably, and it was found that the acid numbers of the sludge-free oils had a linear relationship with the percentage carbon in the paraffinic structure of the original oil. Thus, it would seem that two types of acid formation took place. One was associated with paraffinic content and resin formation, and the other with aromatic content and sludge formation.

Figure 11 shows that there was no relationship between the density increase after 24 hours oxidation and the aromatic content but that there was

the resins was dependant upon the paraffinic content of the original oil. Oil number 1 produced soluble sludge but no insoluble sludge, the soluble sludge from Oil number 1 having a greater acidity than that from Oil number 4 which did produce insoluble sludge. Insoluble sludge was found to be much more acidic than either soluble sludge or resins.

Resins formed from all three oils tended towards constant values of density, with those of Oil number 4 greater than those of Oil number 1, which in turn was greater than the resins from Oil number 2. This was also the order of the densities of the original oils, but the densities of the resins were greater than those of the oils. The density of the soluble sludge formed from Oil number 1 tended to increase with oxidation time, whereas the soluble sludge formed by Oil number 4 rapidly attained a constant value.

The molecular weights of all resins tended towards values which were only slightly greater than those of the original oils, with Oil number 4 showing the greatest difference between the molecular weight of resin and that of the oil. Since the molecular weights are very similar to those of the original oils it would appear that very little polymerisation took place during the formation of resins, but that Oil number 4 showed a greatest tendency to polymerise - probably due to the high aromatic content of Oil number 4. After initial very high values, the molecular weights of soluble sludge decreased and tended towards constant values which were much higher than those of the original oils and the resins. This indicated that polymerisation played a large part in the formation of soluble sludge. The decrease in molecular weight of soluble sludge may be partially due to absorption of resins on to the surface of the sludge when it was being precipitated by n-pentane.

some relationship between the increase in density of the filtered oils and the total number of rings per molecule. Desludging the oxidised oils reduced the value of the density considerably, and when the resins were removed the density became less than those of the original oils.

Insoluble sludge was found to be more acidic than soluble sludge, which in turn was more acidic than resins. In the case of Oil number 1 the soluble sludge had a higher acid number than the soluble sludge from Oil number 4, which had also produced insoluble sludge. The acidity of resins in Oil number 2 was still increasing after 24 hours oxidation, and tending to become greater than that of either Oil number 1 or Oil number 4. Hence it would seem that the acidity of resins was lost in the formation of soluble sludge, which in turn lost its acidic material in the formation of insoluble sludge.

The resins formed by all three oils have approximately the same value of carbon residue, but this value was less than that of the sludges. Insoluble sludge had a lower carbon residue than soluble sludge which suggests that no further polymerisation took place after formation of soluble sludge, and that further oxidation of soluble sludge produced compounds which are more easily cracked and vaporised. This agreed with the work of Gruse and Livingstone (114) who showed that in the thermal coking of hydrocarbons under essentially non-oxidising condition, the greater the number of rings per molecule then the greater the carbon residue.

The acid numbers of the resins from Oil number 1 and 4 tended to be more constant than those from Oil number 2, which was still increasing after 24 hours oxidation. After this time it would seem that the acid number of

The properties of the resins formed during the course of the present investigation are very similar to those of the original oils, but tending to have higher values of density, molecular weight, acidity, and carbon residue. Soluble sludge appeared to have higher values of density, molecular weight, acidity and carbon residue than the resins indication that soluble sludge was a more oxidised and polymerised material than resins. Desludged oils had characteristics approaching those of the original oils, whereas deresined samples generally had lower values of density, molecular weight, etc. than the original oils. Hence the material suffering greatest oxidative attack must be the heavier and more viscous compounds present in the unoxidised oils.

Haus (101) found that resins preformed and separated from lubricating oils were similar in molecular weight and elemental composition to the resins formed during oxidation. It has also been claimed (102) that the ultimate analyses of sludge, resins and polycyclic hydrocarbons of high molecular weight are all very similar, and hence the chemical structure of resins and sludge are similar, only their physical and physical-chemical properties showing any real differences. It is also thought (102) that the resins present in unoxidised oils have a small number of paraffinic side chains, and this should be true for resins formed by oxidation assuming that Haus (101) is correct.

The information gleaned during the course of the present work has agreed with that in the literature (60,101,90,114) in showing that the oxidation of a lubricating oil takes place as follows:

hydrocarbons $\rightarrow$ resins $\rightarrow$ soluble sludge $\rightarrow$ insoluble sludge

When the three oils employed in this investigation were oxidised it was found that Oil number 1 produced soluble sludge and resins, Oil number 2

produced resins only, and Oil number 4 produced insoluble sludge, soluble sludge and resins. Where resins only were formed it was found that their rate of formation was linear up until about 18 hours, whereupon the rate increased sharply. The formation of resins in Oil number 1 exhibited a linear rate until 9 hours oxidation, after which the rate of formation decreased. This decrease in the rate of formation coincided with the formation of soluble sludge, which was produced at an increasing rate. The rate of formation of soluble sludge in Oil number 1 was equal to the rate of decrease in the formation of resins. In the case of Oil number 4 there was a very rapid initial increase in resin formation, the rate of which then decreased till a more or less constant value was obtained. During this time the formation of soluble sludge increased rapidly at first and then slowed down, while the production of insoluble sludge proceeded at a constant rate. This indicated that equilibrium had been reached in the formation of insoluble sludge from soluble sludge, and soluble sludge from resins.

The densities of the resins from Oils 2 and 4 tended towards a constant value, but in the case of Oil number 1 the density of the resins tended to decrease. This coincided with a steady increase in the density of the soluble sludge formed by this oil. Similarly, the soluble sludge from Oil number 4 showed a slight decrease in density, indicating that the denser material was being transferred to the insoluble sludge. Thus it would appear that the denser material was being transferred from resins to insoluble sludge via soluble sludge.

Where no sludge was formed the acid number of the resins tended to increase with oxidation time, but where soluble sludge was also formed the acidity of the resins tended towards a constant value. In the case of

Oil number 1 the acidity of the soluble sludge increased with increasing oxidation time. This indicated that the more acidic material from the resins was being converted into soluble sludge. Oxidation of Oil number 4 gave resins and soluble sludge which tended towards constant acidity, but also gave insoluble sludge which had an increasing acidity as oxidation progressed. Once again it would appear that a transfer of material was taking place from soluble to insoluble sludge.

There does not appear to be much doubt that oxidation of lubricating oil hydrocarbons result in resin formation, followed by soluble sludge and eventually insoluble sludge. There appears to be a uniform series of products from the true oil to insoluble materials (90,61). Since there appears to be little or no fundamental difference between resins and sludges (both soluble and insoluble) one wonders what property causes the sludges to be precipitated from low boiling paraffins, whereas resins are not. Further, what causes the insoluble sludge to be precipitated in the lubricating oil medium?

In the first steps in the oxidation of a mineral lubricating oil seems to be the conversion of the heavier hydrocarbon molecular, by a comparitively light oxidative attack, to resins. Further oxidation of these resins occurs, and then polymerisation and condensation takes place with the formation of soluble sludge. The union of aromatic carbonyl and hydroxyl materials by condensation is probably the main reaction in the oxidative polymerisation of the resins. This would also account for the fact that any oxidised oil forming a soluble sludge also produced resins with a fairly constant acid number.

A decrease in the average molecular weight of soluble sludge, after initial very high values, was observed which may have been due to adsorption

of resins on to the surface of the sludge. It has been shown elsewhere (115) that residual oils produce sludges at high temperatures which are peptised by the resinous materials, resulting in the formation of asphaltic systems. Distillate oils, low in resins, produce sludges which formed into heterogeneous particles having little effect upon the properties of the oil. It has been found (102) that the resins formed true solutions in oxidised oils, whereas sludges were dispersed colloidally, probably due to the peptising effect of adsorbed resins and heavy polycyclic hydrocarbons. The peptising properties of resins have also been observed by Katz and Beu (105).

Sludges are dispersed colloidally in aromatic hydrocarbons but tend to aggregate and precipitate in paraffinic hydrocarbons, e.g. they are colloidally dispersed in the lubricating oils from which they are derived by oxidation, but are precipitated by addition of an excess of petroleum ether. Thus, sludges appear to be lyophobic with respect to paraffins, but lyophibic with respect to aromatic hydrocarbons. This is of course the principle of the method which has been commonly employed in sludge separation (62). Adsorption of resins on to the surface of the colloidal sludge particles gives the particles protection against coagulation brought about by the lyophobic materials present in the oils. Sludge suspensions can also be formed in lubricating oils, and this is probably due to an insufficient concentration of peptising material.

Insoluble sludges are known, and this has been further demonstrated in this work, to have high acid number, and hence they have a high polarity compared with that of the lubricating oil medium. This is, therefore, the probable cause of insoluble sludge precipitation, and hence the further oxidation of soluble sludge changes its properties to such an extent that it is no longer soluble. The change in the nature of the soluble sludge could be due

to the oxidation of the adsorbed resins to soluble sludge.

Since the formation of sludge apparently requires the presence of aromatics, and it is well known that aromatics oxidise to hydroxy acids which are insoluble in petroleum oils (102), it would seem that the above explanation of the solubility of oil insoluble sludge is perfectly feasible.

It would appear that for lubricating oils of low aromatic content, i.e. 7 or 8%, there was a sufficient amount of aromatic hydroxy compounds being formed to condense with aromatic carbonyl compounds (95) to form sludges. When the oil had about 8% aromatics there appears to have been a sufficient amount of inhibitor present to suppress the formation of aromatic hydroxyl compounds. These inhibitors were probably compounds similar to naphthols, the inhibiting effects of which have been well described in the literature (48,61). As the amount of aromatics increased there seemed to be an excess of hydroxyl compounds formed so that the formation of inhibitor had little effect and the formation of sludge proceeded as before. As the percentage of aromatic carbon in the lubricating oil increases further the aromatic hydroxyl compounds are in excess of the aromatic carbonyls and hence could cause the precipitation of the soluble sludge as oil insoluble sludge.

The repeated oxidation, recovery and re-oxidation of a high aromatic oil for several periods of time (up to 24 hrs say) could be a programme of work with several interesting possibilities. One such possibility may be the eventual complete breakdown of the oil and analysis of sludges, resins and composition of the de-resined oils could provide further clues to the oxidation path of the oil. Since, however, the material being removed upon oxidation was apparently aromatics there would also be the possibility that when the "optimum aromatic : naphthenic ratio" had been achieved in the recovered oil

the oxidation process would be inhibited. This could also be tackled from another angle - what is the effect upon sludge formation of "pure" compounds which give rise to naphthols, phenols, carbonyl compounds, etc, when oxidised?

CHAPTER X

CHAPTER X

Deterioration in the Internal Combustion Engine

1. General

The four oils already oxidised by means of the I.P. test were deteriorated in the Pelapone I.C. engine for various periods of time (up to 120 hrs) On removal from the crankcase, the oil sample was placed in a vacuum over at 120°C and 29.5" Hg. for one hour to remove any traces of engine fuel. This treatment was found to be effective in removing the gasoline without altering the characteristics of the deteriorated oil. The oil sample was then filtered through an asbestos-packed Gooch crucible and the chloroform insoluble, oil insoluble, and oil soluble materials were determined as described in the Appendix.

2. Extent of Deterioration

From figures 29,30,31 and 32 it can be seen that the order of oxidation stability under engine conditions was the same as that shown by the oils when oxidised by the modified Institute of Petroleum test, i.e. Oil No. 2 > Oil No. 1 > Oil No. 3 > Oil No. 4. Thus, in this case, the change of oxidation conditions and the presence of metallic catalysts have not been such as to alter the order of oxidation stability. Again it is seen that oxidation stability is not directly proportional to the percentage of aromatics in the original oil, since Oil number 2 suffers less oxidation, even though it contains more aromatics, than Oil number 1. Although the four oils were in the engine crankcase for five times as long as they were in the I.P. oxidation cell, the amount of sludge and resins formed was much less than in the I.P. test.

The chloroform insoluble material, i.e. the material not produced by deterioration of the oil, was a direct function of the time spent in the engine.

FIGURE 29

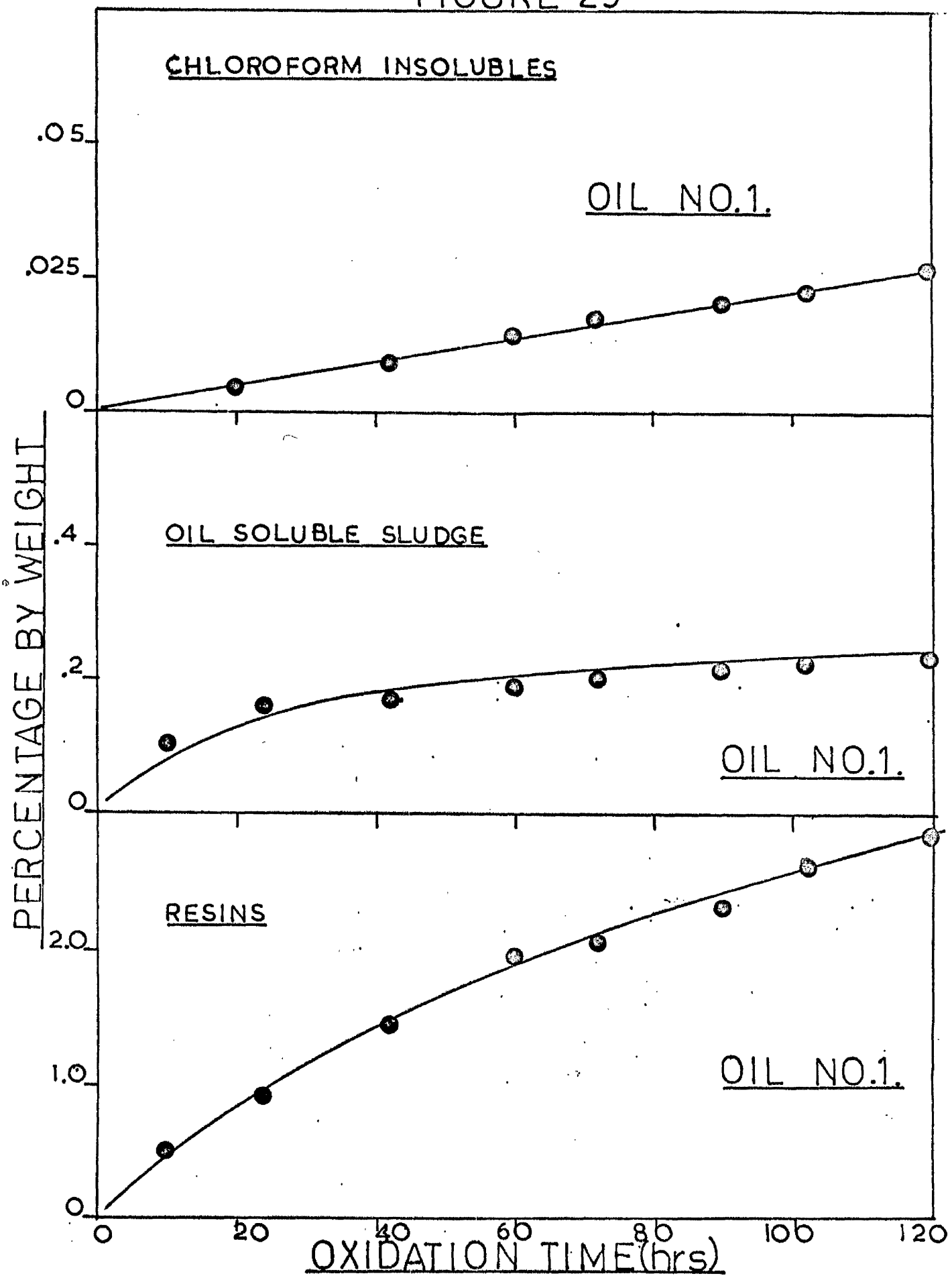

CHLOROFORM INSOLUBLES
.05
.025
0
OIL NO.1.
OIL SOLUBLE SLUDGE
.4
.2
0
OIL NO.1.
RESINS
2.0
1.0
0
OIL NO.1.
PERCENTAGE BY WEIGHT
0
20
40
60
80
100
120
OXIDATION TIME(hrs)

FIGURE 30

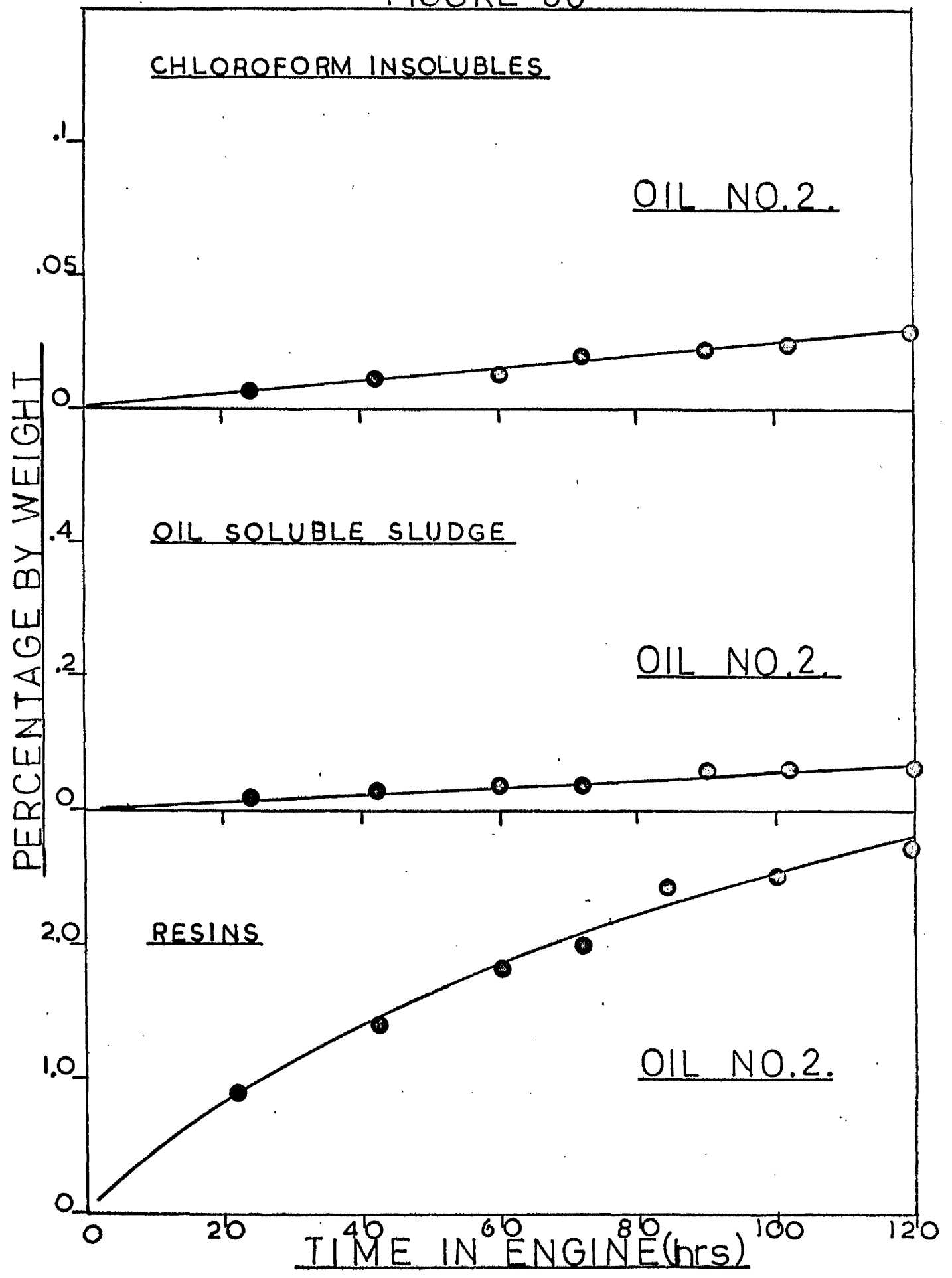

CHLOROFORM INSOLUBLES
.1
.05
0
OIL NO.2.
OIL SOLUBLE SLUDGE
.4
.2
0
OIL NO.2.
RESINS
2.0
1.0
0
OIL NO.2.
PERCENTAGE BY WEIGHT
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 31

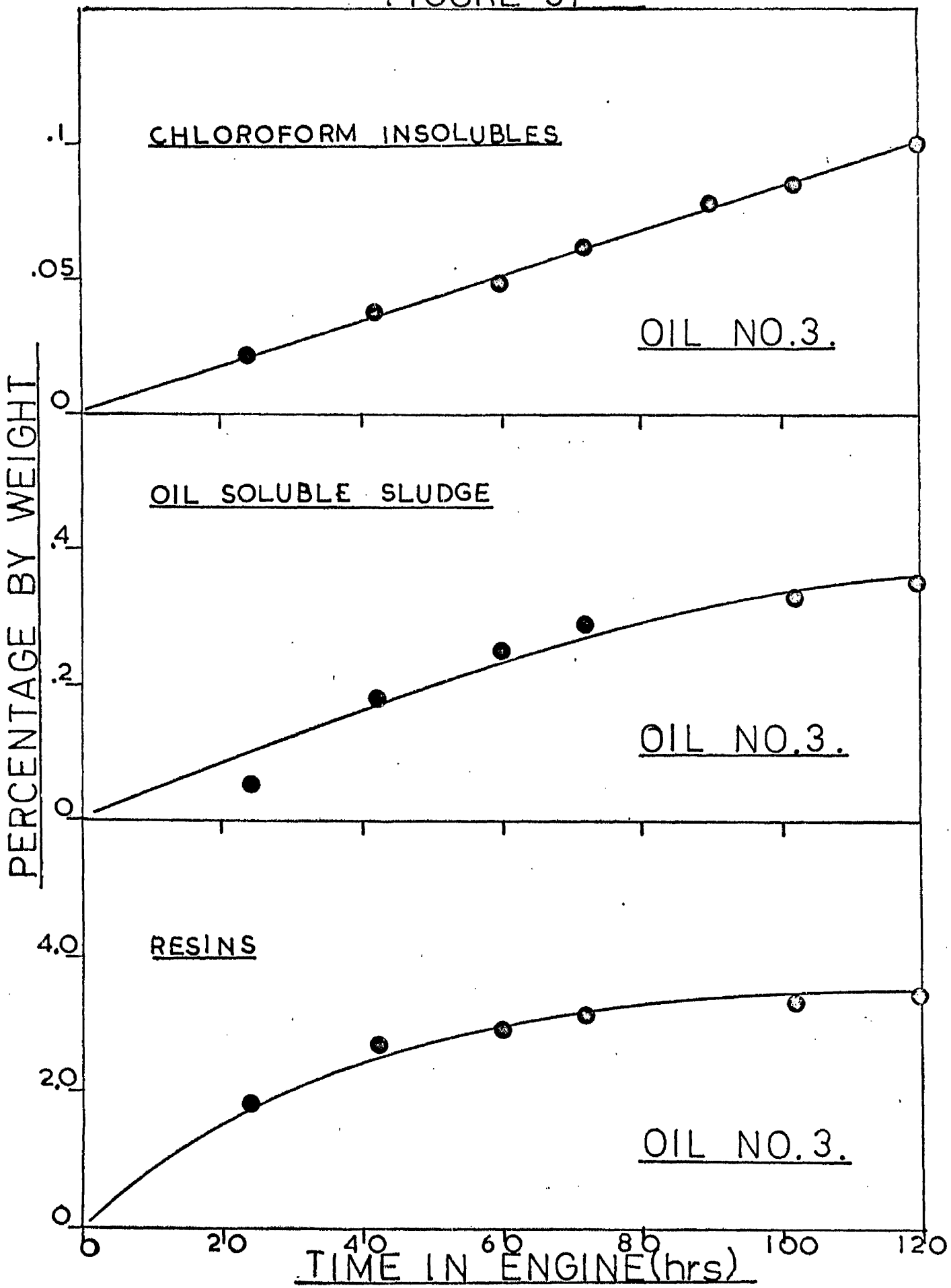
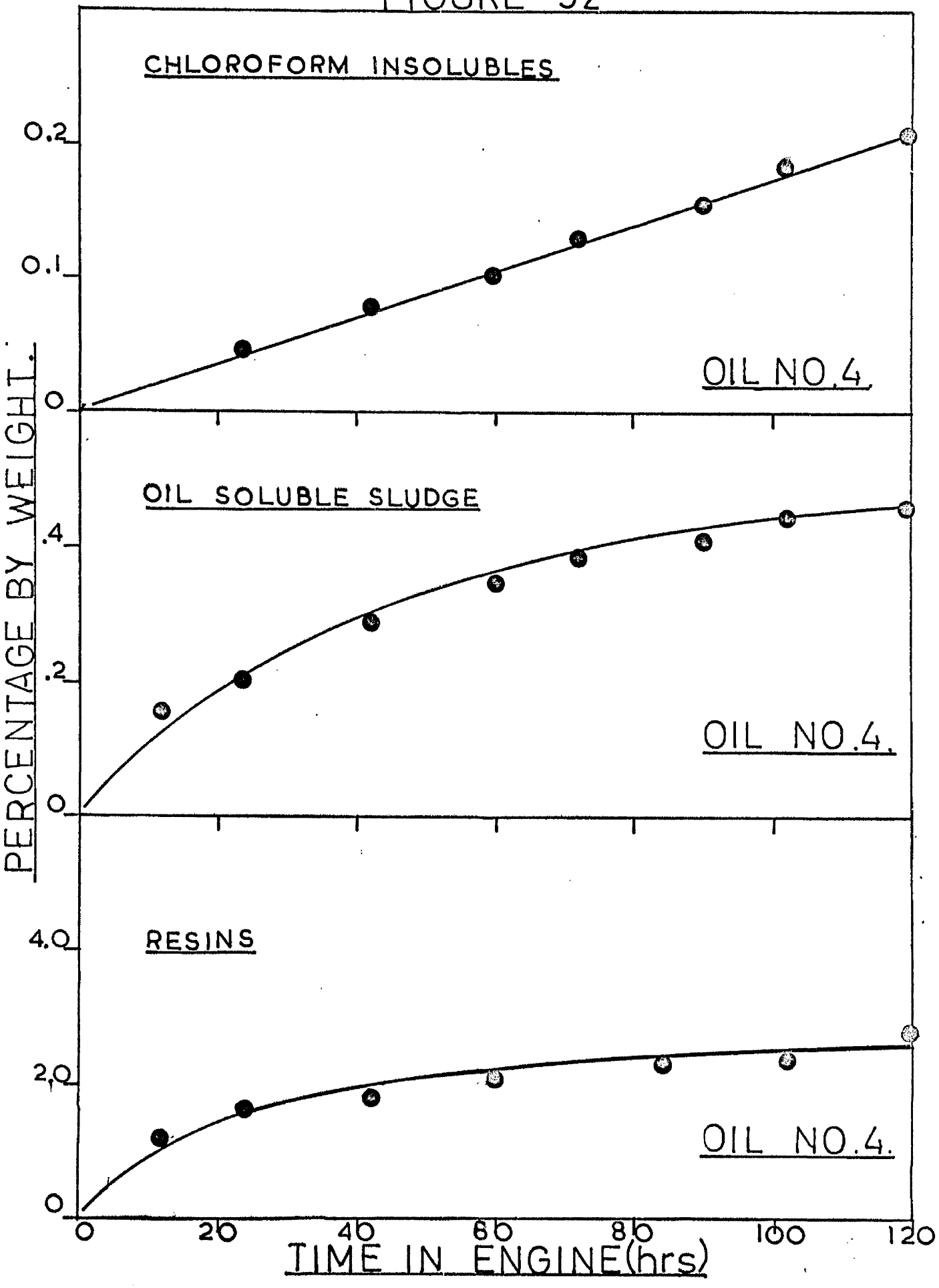

CHLOROFORM INSOLUBLES
.1
.05
0
OIL NO.3.
OIL SOLUBLE SLUDGE
.4
.2
0
OIL NO.3.
RESINS
4.0
2.0
0
OIL NO.3.
PERCENTAGE BY WEIGHT
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 32


CHLOROFORM INSOLUBLES
0.2
0.1
0
OIL NO.4.
OIL SOLUBLE SLUDGE
.4
.2
0
OIL NO.4.
RESINS
4.0
2.0
0
OIL NO.4.
PERCENTAGE BY WEIGHT.
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

The four oils did not give the same amount of chloroform insolubles after 120 hours, the greatest amount of these insolubles being found in the oil which suffered the greatest deterioration. This was probably due to greater wear and corrosion of the metal parts of the engine by sludge and acidic materials formed in the oxidised oils.

Unlike their behaviour in the I.P. oxidation test all four oils produced oil soluble sludge. Oil number 2 gave no such material when oxidised under the I.P. conditions, but when deteriorated in the Pelapone engine a small amount of soluble sludge was produced. This may have been due to the presence of catalysts in the engine or to the higher temperatures encountered in the combustion chamber. Whereas Oil number 2 shows a slightly advanced state of oxidation, Oil number 4 shows a lower degree of oxidation since it does not produce insoluble sludge when deteriorated in this engine. The total amount of sludge formed by each oil was in agreement with the oxidation stability exhibited by each oil under the modified I.P. test condition, and once again an optimum aromaticity was observed.

The oils which showed the greatest oxidation stability under the I.P. test conditions formed resins fairly rapidly at first under the engine conditions, and then the rate of formation decreased slightly. The more stable oils (1 and 2) showed a more constant rate of resin formation than did oils (3 and 4). Conditions in the engine seemed to favour resin formation rather than sludge formation since the oils which produced most sludge had a proportionately higher resin content after 120 hours in the Pelapone engine.

3. Acid Formation

All the samples deteriorated in the engine were much less acidic than those samples oxidised by air-blowing. The chloroform insolubles showed some

FIGURE 33

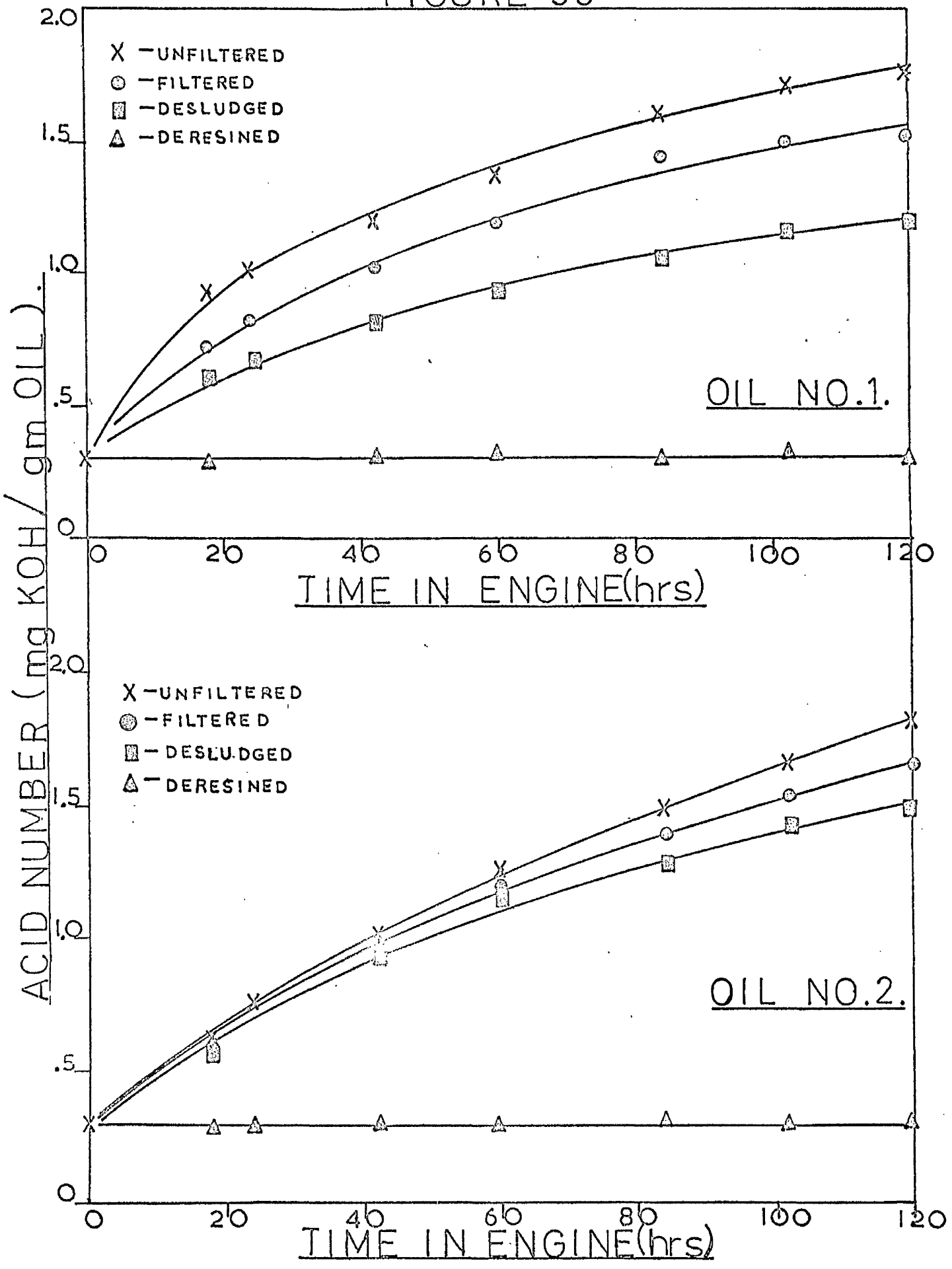
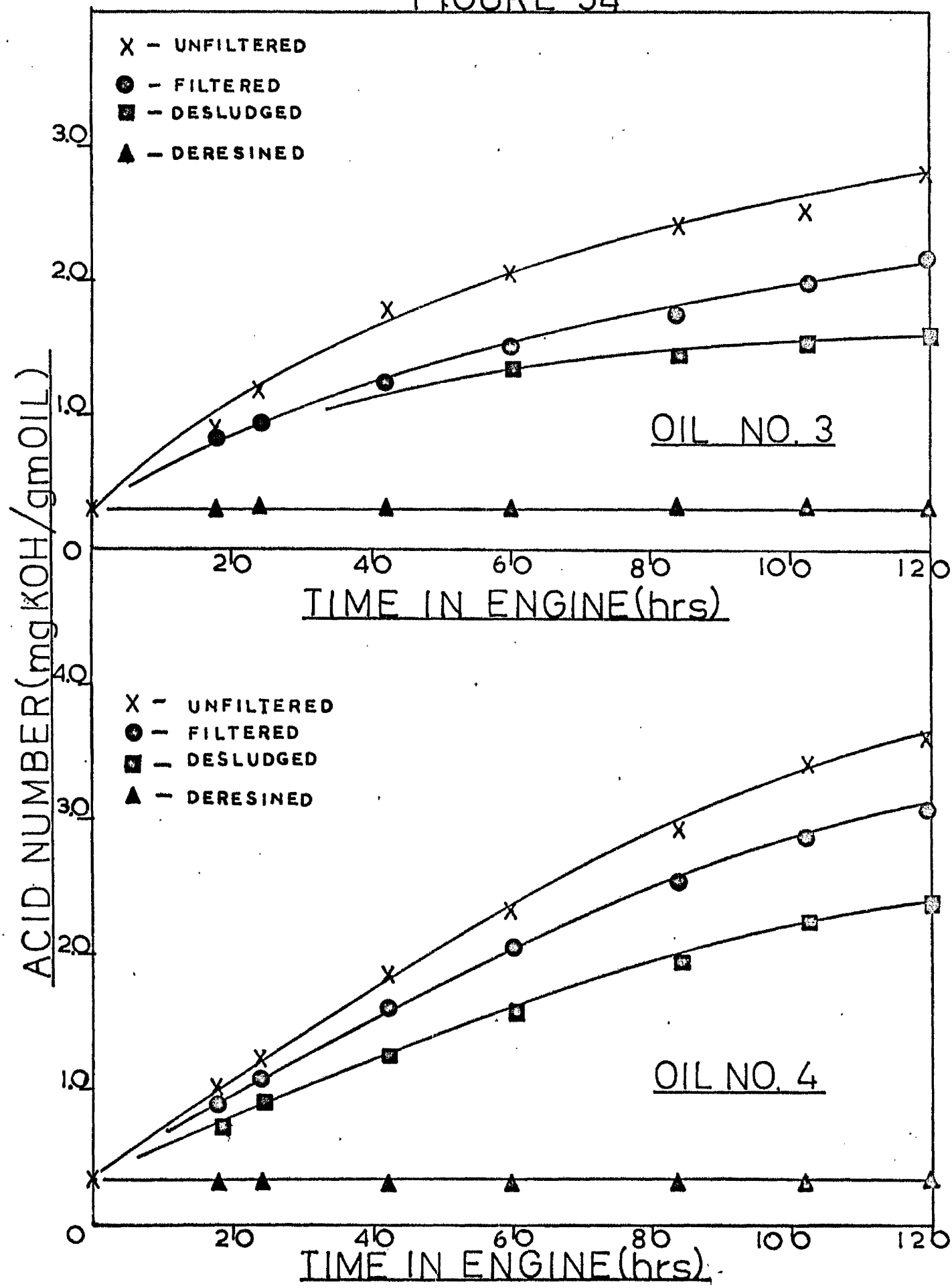

X —UNFILTERED
⊙ —FILTERED
▣ —DESLUDGED
△ —DERESINED
OIL NO.1.
TIME IN ENGINE(hrs)
X —UNFILTERED
⊙ —FILTERED
▣ —DESLUDGED
△ —DERESINED
OIL NO.2.
TIME IN ENGINE(hrs)
ACID NUMBER (mg KOH/gm OIL).
0
.5
1.0
1.5
2.0
0
20
40
60
80
100
120

FIGURE 34


X – UNFILTERED
– FILTERED
– DESLUDGED
– DERESINED
3.0
2.0
1.0
0
ACID NUMBER (mg KOH/gm OIL)
OIL NO. 3
2.0
4.0
6.0
8.0
10.0
12.0
TIME IN ENGINE (hrs)
X – UNFILTERED
– FILTERED
– DESLUDGED
– DERESINED
4.0
3.0
2.0
1.0
0
OIL NO. 4
2.0
4.0
6.0
8.0
10.0
12.0
TIME IN ENGINE (hrs)

acidity but this may be due to combustion products of the fuel. Filtration removed these particles and it can be seen from figures 33 and 34 that the acidity was reduced by an amount proportional to the amount of chloroform insolubles retained by each oil.

Desludging the oil also reduced the acidity and again the reduction was proportional to the amount of sludge formed by the oil. A similar effect was observed when the oil samples were deresined, the acid numbers being reduced to value the same range as those of the original oils.

In contrast to their behaviour in the modified I.P. test, the total acidity developed by the oils when in the engine was greatest in the oils containing the greatest amount of aromatics.

From figure 35 it is clear that the soluble sludge formed by Oil number 1 had a lower acid number than that formed by this oil in the I.P. test - even after attaining a maximum value after about 102 hours use. Oil number 2 gave a soluble sludge which had the highest acidity of all the samples produced by deterioration in the engine, but since no soluble sludge was produced by this oil in the I.P. test no comparison can be made. Oil number 4 produced a soluble sludge which had much the same order of acidity as that of Oil number 1 but tended towards a constant value which was higher than that of the sludge from Oil number 1 after 120 hours deterioration. On the other hand, Oil number 3 gave a sludge which showed increasing acidity as the time spent in the engine increased.

In general, resins had lower acid numbers than those possessed by the resins formed during air-oxidation. The resins formed in the Pelapone engine showed acidities which tended towards constant values, and as in the case of

FIGURE 35

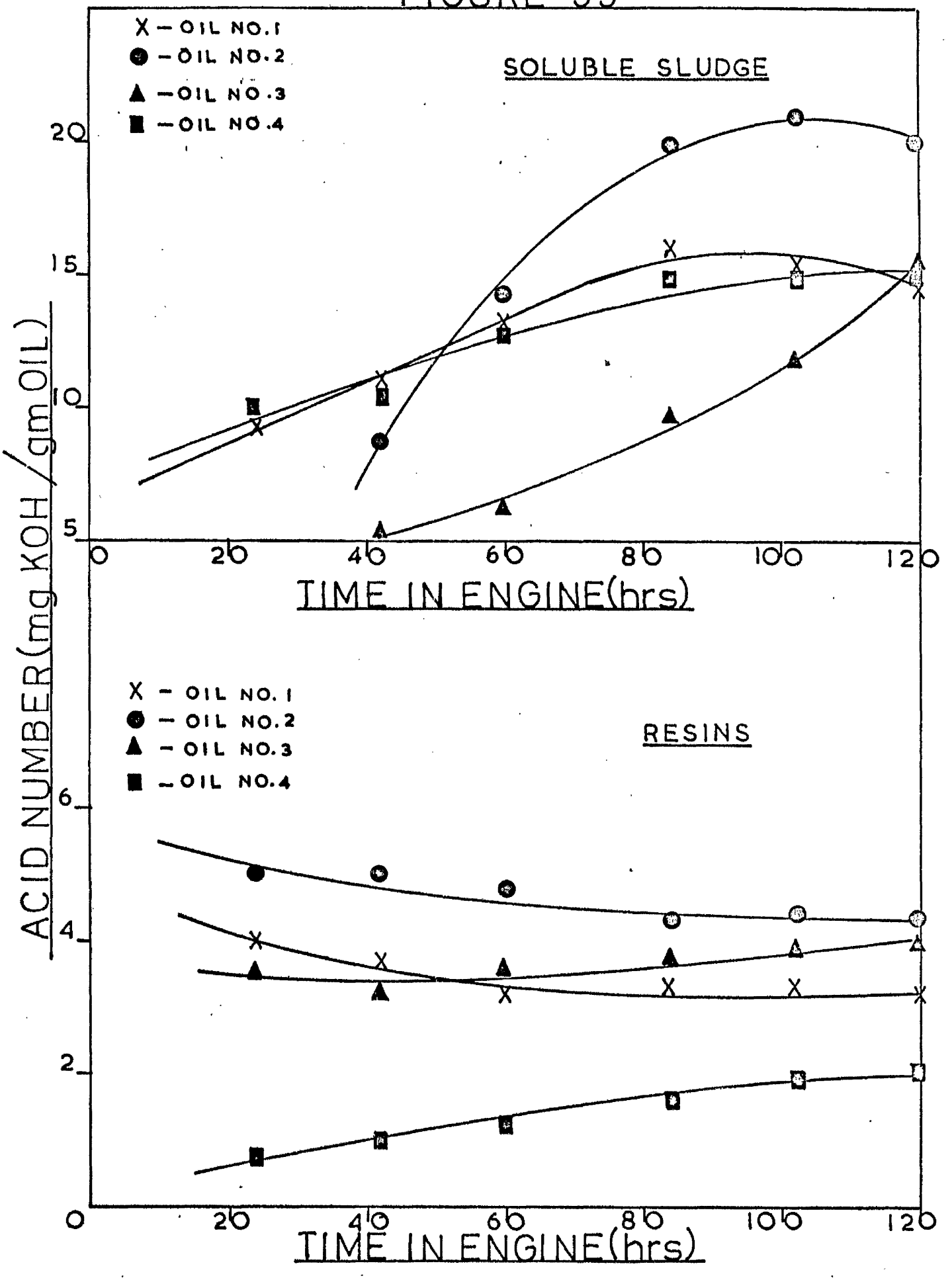
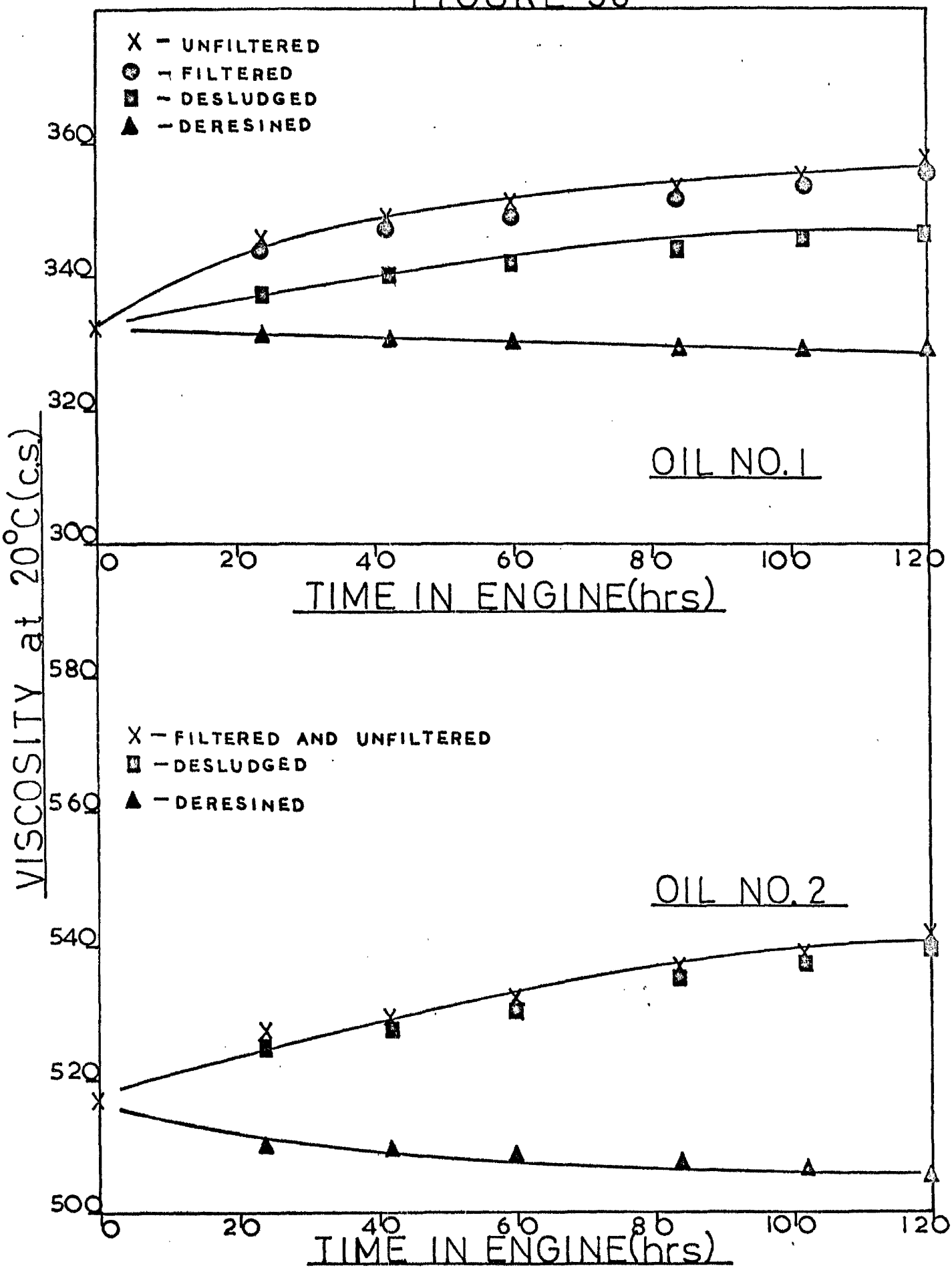

X – OIL NO.1
● – OIL NO.2
▲ – OIL NO.3
■ – OIL NO.4
SOLUBLE SLUDGE
20
15
10
5
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
ACID NUMBER(mg KOH / gm OIL)
X – OIL NO.1
● – OIL NO.2
▲ – OIL NO.3
■ – OIL NO.4
RESINS
6
4
2
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 36


X – UNFILTERED
– FILTERED
– DESLUDGED
– DERESINED
360
340
320
300
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
OIL NO. 1
VISCOSITY at 20°C (c.s.)
580
560
540
520
500
X – FILTERED AND UNFILTERED
– DESLUDGED
– DERESINED
OIL NO. 2
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

the soluble sludge, the resins formed by Oil number 2 had the highest acidity. The resins from Oil number 3 had the second greatest acid number, followed by those from Oil number 1 and then by those of Oil number 14.

4. Viscosity

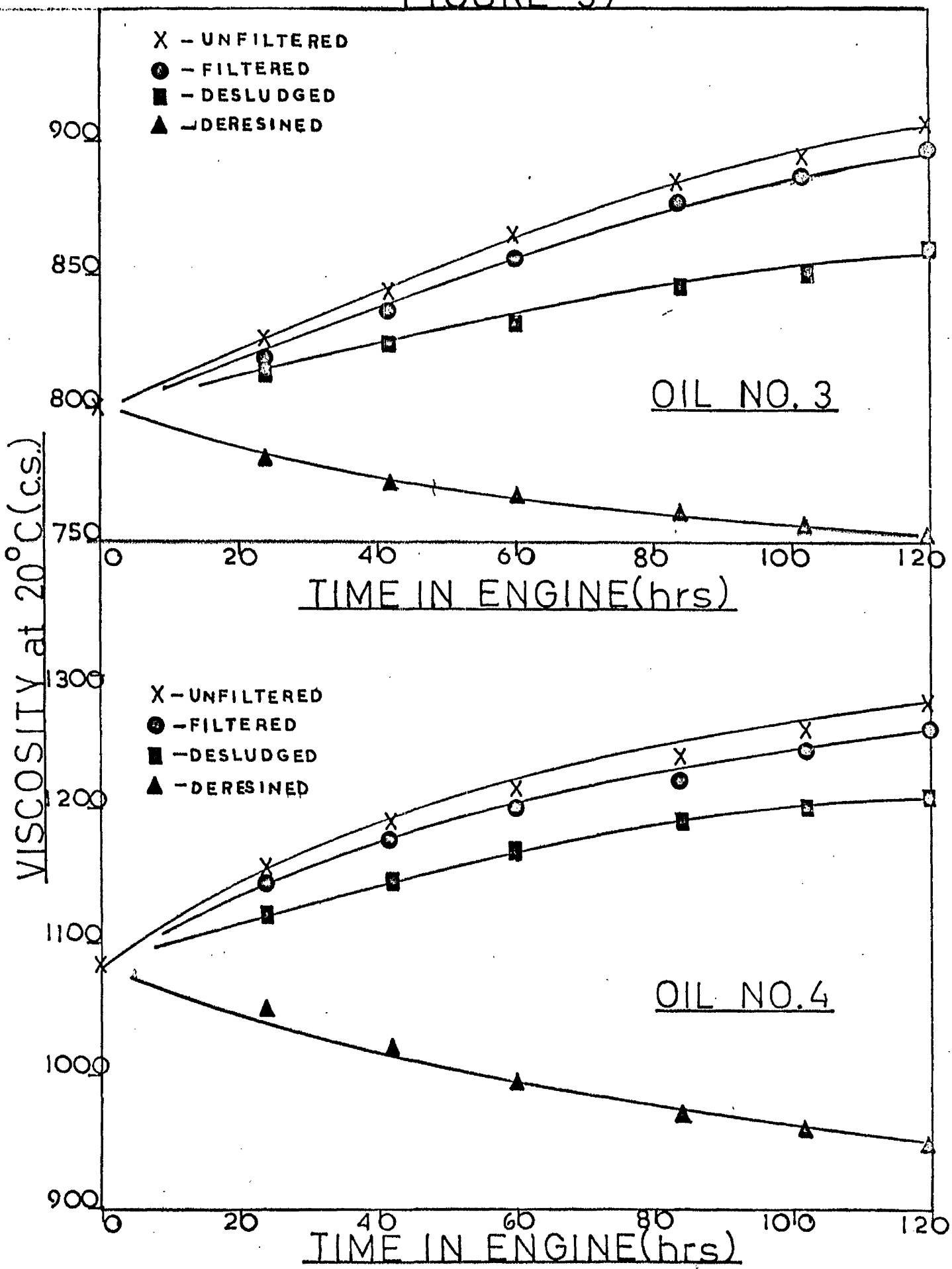
The effect of deterioration, by use in the engine, on the viscosity of the four oils is illustrated in figures 36 and 37. It can be seen that the presence of chloroform insolubles increased the viscosity of the oil in proportion to the amount of insolubles produced. Thus, the oils which produced the greatest amount of engine wear and corrosion products also suffered the greatest increases in viscosity.

As before the desludging of the samples by n-pentane treatment decreased the viscosity, and the amount of decrease was apparently proportional to the amount of soluble sludge removed. The viscosities of the desludged oils were still greater than those of the original oils. Similarly, deresining the oils reduced the viscosity - to values below that of the original oil. The oils which produced the largest amount of resins also gave the greatest decrease in viscosity when these resins were removed by fuller's earth.

The greatest increases in viscosity were observed in the oils which produced the greatest amount of oxidation products. Thus Oil number 2 showed the least change in viscosity followed by Oil number 1, Oil number 3 and Oil number 4 this was in general agreement with the findings of the results of the air-oxidation experiments.

In the deterioration of these oils by means of the Pelapone engine it was observed that resins contributed by far the most to the total viscosity increase, unlike the results obtained in the modified I.P. test in which the

FIGURE 37


X – UNFILTERED
● – FILTERED
■ – DESLUDGED
▲ – DERESINED
900
850
800
750
0
20
40
60
80
100
120
OIL NO. 3
TIME IN ENGINE(hrs)
VISCOSITY at 20°C (c.s.)
1300
1200
1100
1000
900
X – UNFILTERED
● – FILTERED
■ – DESLUDGED
▲ – DERESINED
OIL NO. 4
TIME IN ENGINE(hrs)

sludge contributed most to the viscosity increase. However, in the I.P. oxidation of these four oils the resins initially contributed the greatest part of the total viscosity increase. In the case of the engine deterioration the resins contribution is probably due to the proportionately greater amount of resins produced, i.e. the resin: sludge ratio is greater in the engine deteriorated samples than in the I.P. oxidised samples.

5. Density

In all four cases the density increased with the time spent in the Pelapone engine, but this was not a linear relationship and tended to show a lower rate of increase in density in the later stages of deterioration. Oil number 4 showed the greatest increase in density, the density increase being related to the degree of deterioration of the oil. The order of density increase was therefore the same as the order of total retained oxidation products formed in the four oils in the engine.

Desludging the deteriorated oils reduced the density, the reduction depending on the quantity of oil soluble sludge formed. The densities of the desludged samples were found to be greater than those of the original unoxidised oils. As with desludging, the removal of resins also reduced the densities, but the values for the recovered oils were lower than those of the original oils. Once again, the greatest decrease in density was found in the oil which produced the greatest amount of resins (figures 38,39,40 and 41).

The densities of the oil soluble sludge and resins were calculated as described previously and the results shown graphically in figures 38,39,40 and 41. It was apparent that the densities of these oxidation products were in the same range as those formed by oxidation in the I.P. test. In general, the densities of the resins were lower than the densities of the oil soluble

FIGURE 38

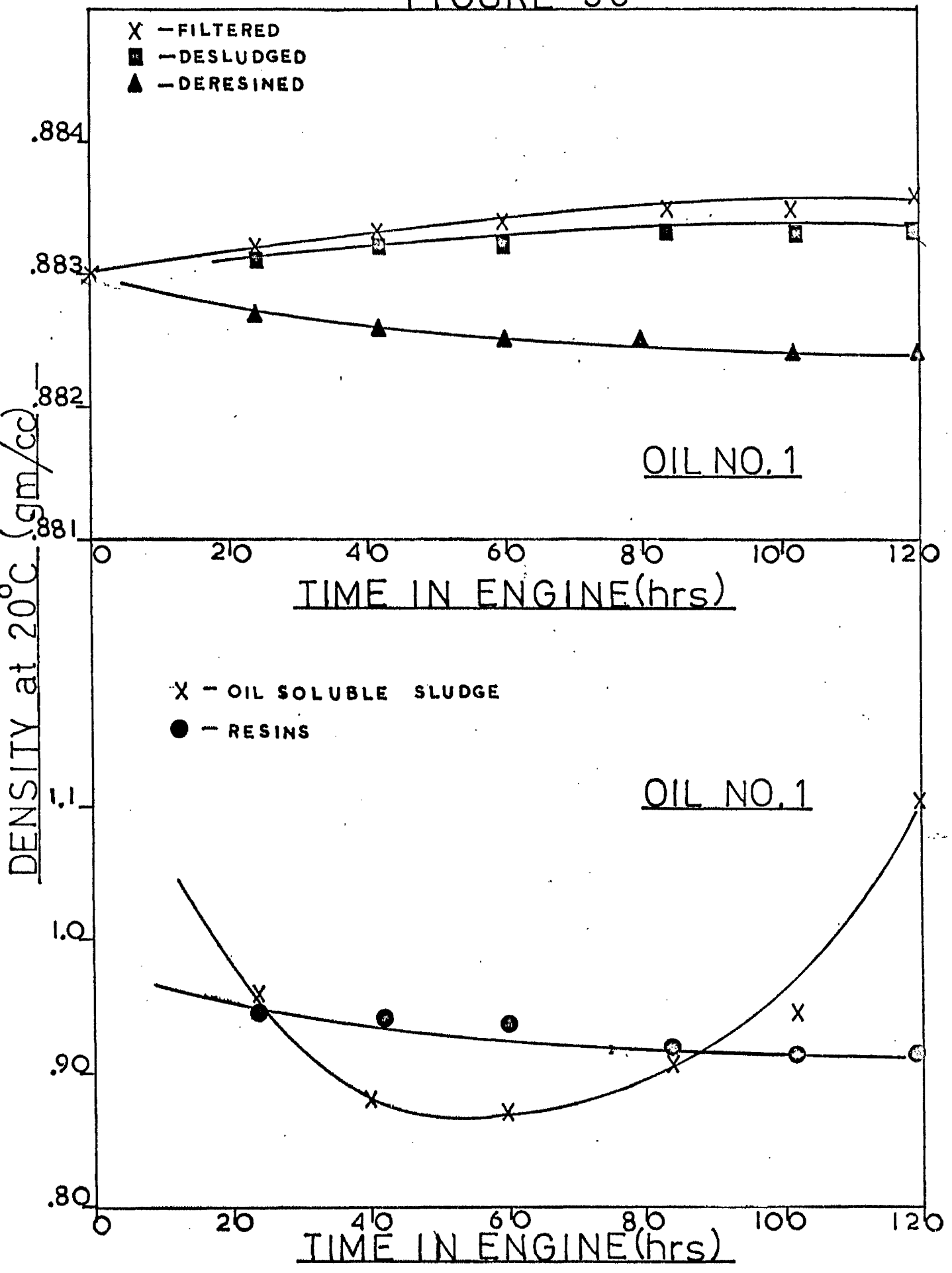

X — FILTERED
■ — DESLUDGED
▲ — DERESINED
.884
.883
.882
.881
OIL NO. 1
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
DENSITY at 20°C (gm/cc)
X — OIL SOLUBLE SLUDGE
● — RESINS
OIL NO. 1
1.1
1.0
.90
.80
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 39

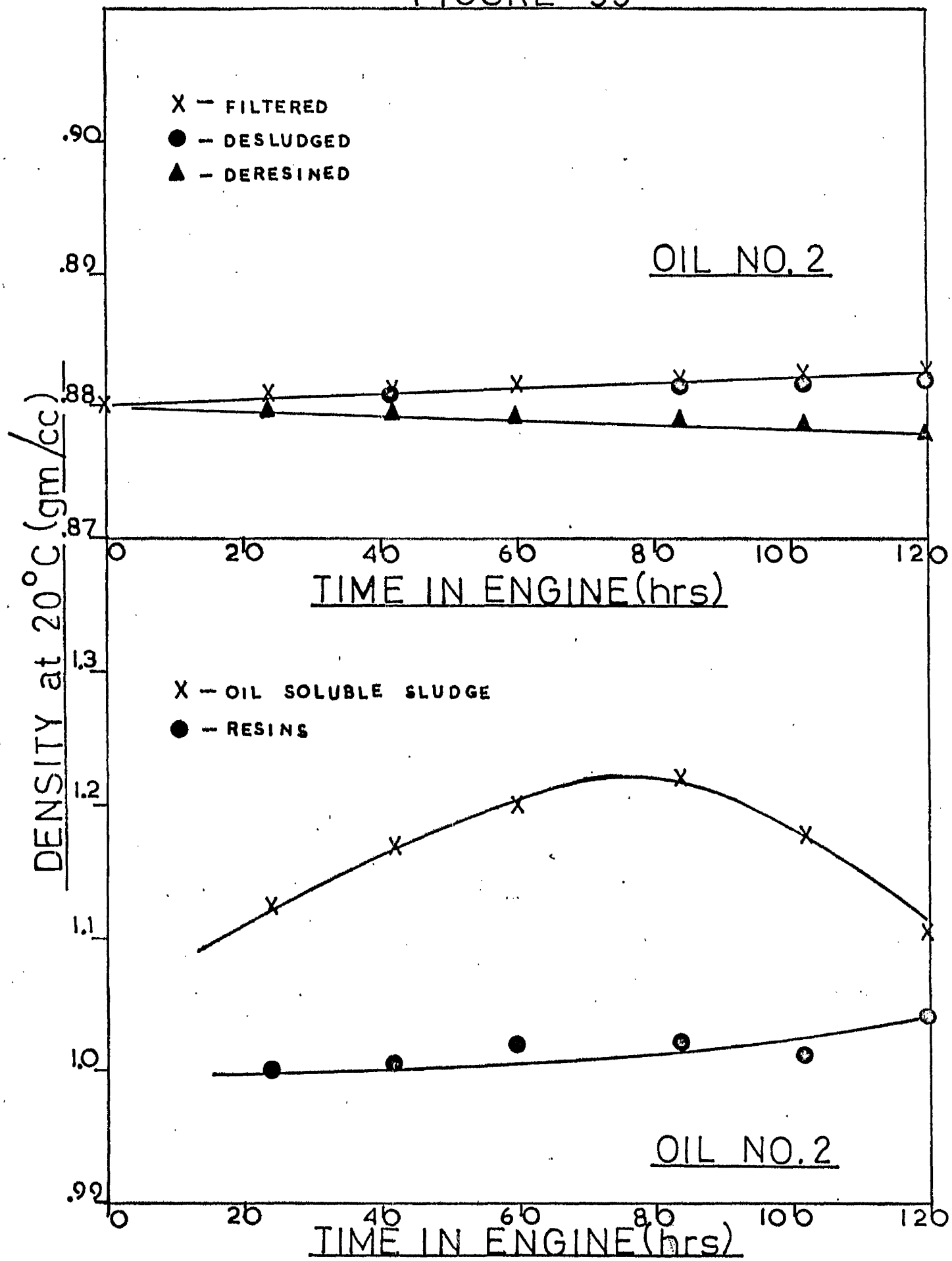

X — FILTERED
● — DESLUDGED
▲ — DERESINED
OIL NO. 2
.90
.89
.88
.87
DENSITY at 20°C (gm/cc)
0
20
40
60
80
100
120
TIME IN ENGINE (hrs)
X — OIL SOLUBLE SLUDGE
● — RESINS
1.3
1.2
1.1
1.0
.92
OIL NO. 2
0
20
40
60
80
100
120
TIME IN ENGINE (hrs)

FIGURE 40

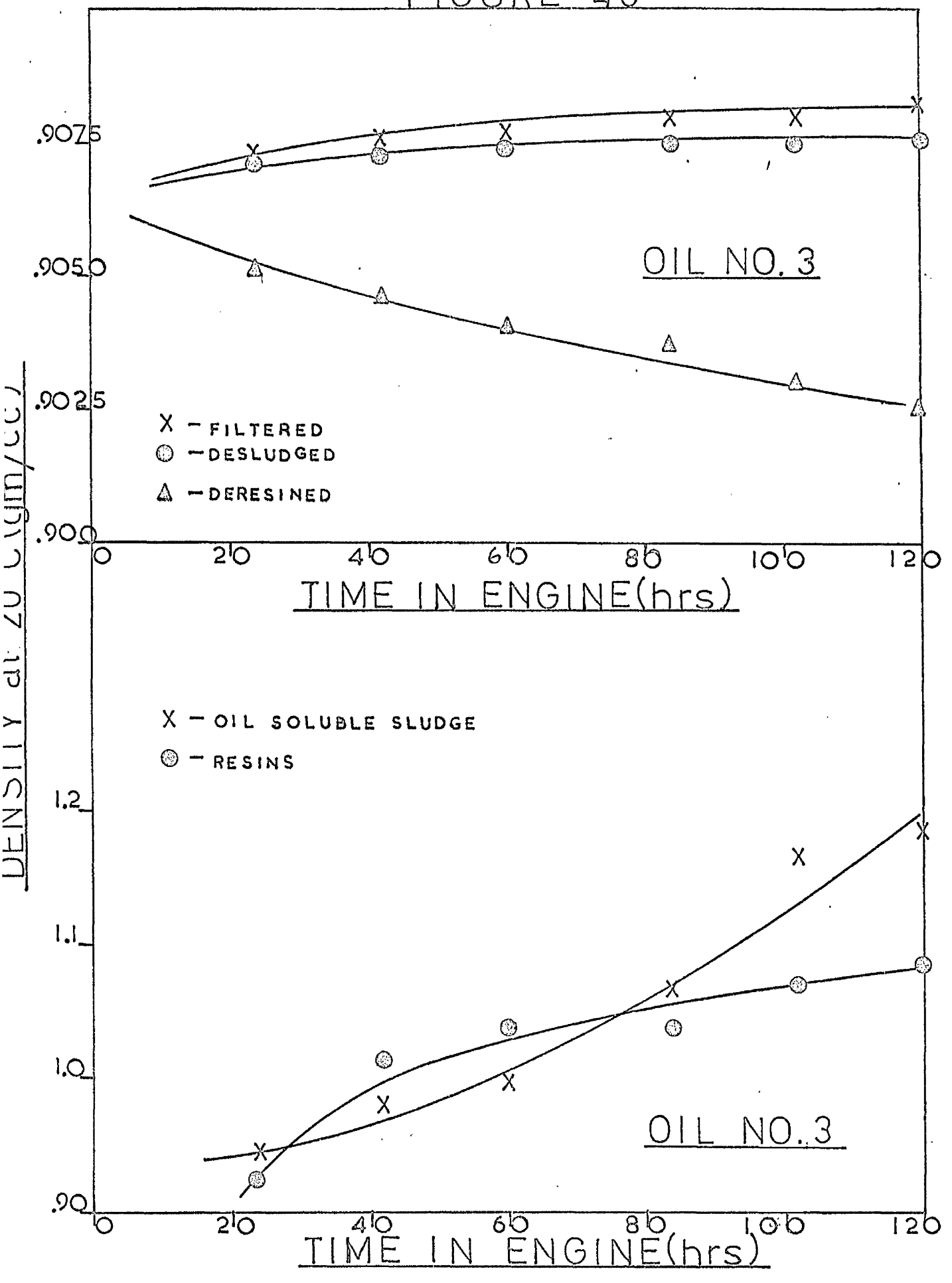
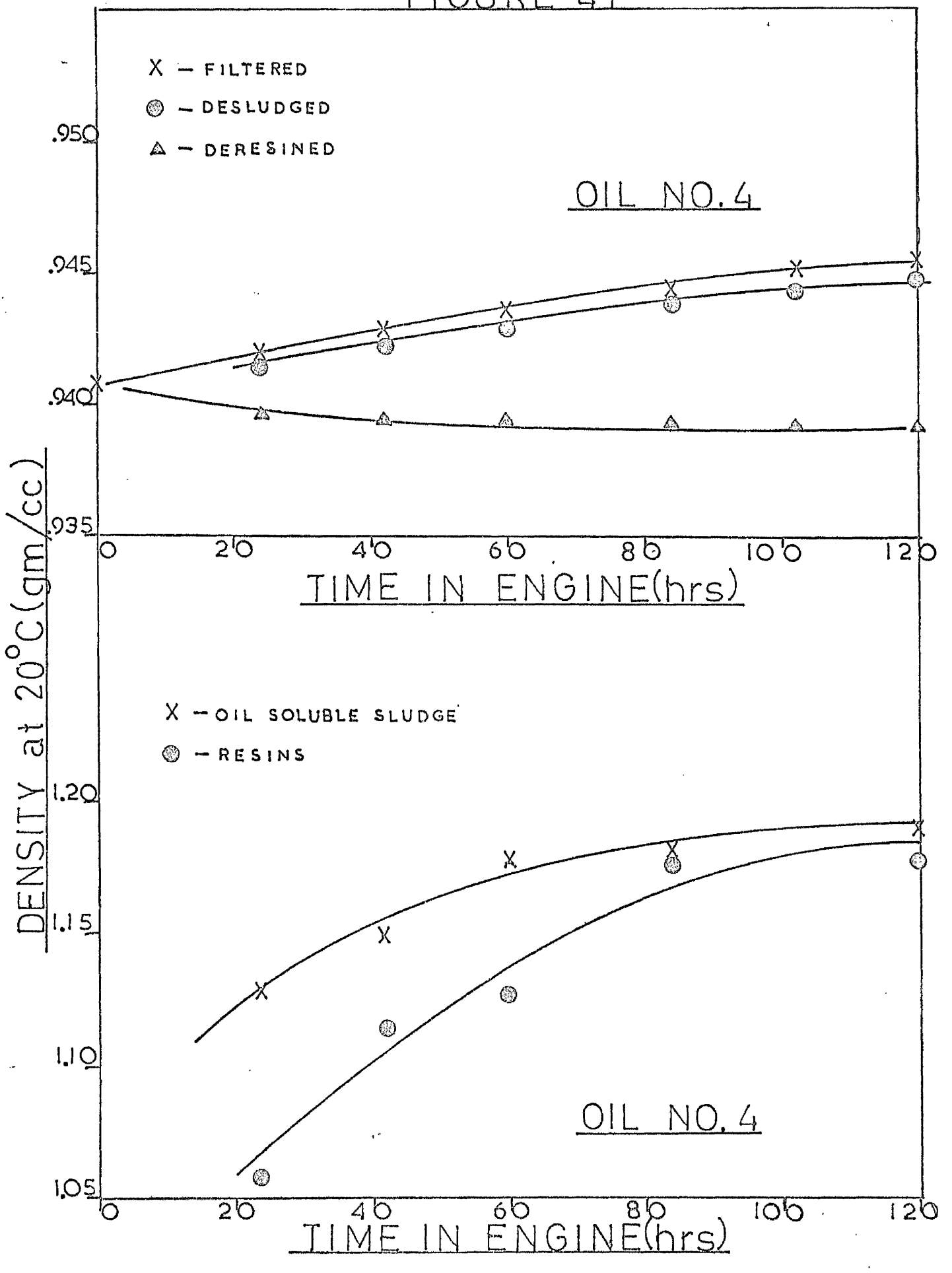

.9075
.9050
.9025
.9000
DENSITY at 20 C (gm/cc)
X – FILTERED
– DESLUDGED
Δ – DERESINED
OIL NO. 3
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
X – OIL SOLUBLE SLUDGE
– RESINS
1.2
1.1
1.0
.90
OIL NO. 3
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 41


X — FILTERED
— DESLUDGED
— DERESINED
OIL NO. 4
.950
.945
.940
.935
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
DENSITY at 20°C (gm/cc)
X — OIL SOLUBLE SLUDGE
— RESINS
1.20
1.15
1.10
1.05
OIL NO. 4
TIME IN ENGINE(hrs)

sludge which also agreed with the previous results. Here, however, the density of the sludge fluctuated more, whereas those of the resins tended towards constant values. It would seem that the equilibrium had not been reached in the engine deterioration of the oil to form oil soluble sludge from resins.

6. Molecular Weight

The graphs shown in figures 42,43,44, and 45 demonstrate the increase in molecular weight of the oils deteriorated in the I.C. engine. The oil which retained the greatest amount of deterioration products also showed the greatest increase in molecular weight. The molecular weights of the samples taken from the crankcase showed no fluctuations as did the samples obtained in the I.P. oxidation test.

Once again it was observed that desludging reduced the molecular weight of the oil in proportion to the amount of soluble sludge removed. The molecular weights of the desludged samples were still greater than those of the original lubricating oils and tended to increase slightly with the time spent in the engine. Similarly, the deresining of the oil samples reduced their molecular weights to values slightly lower than those of the original oils. The molecular weights of the deresined oils decreased slightly with time.

Oil soluble sludge and resin molecular weights were calculated as before, and it was found that the molecular weights of these deterioration products were in the same range as those formed by air-oxidation (figures, 42,43,44 and 45). As before, the soluble sludge molecular weight was greater than that of the resins and this was so in the case of each oil. Both soluble sludge and resin molecular weights tended towards constant values

FIGURE 42

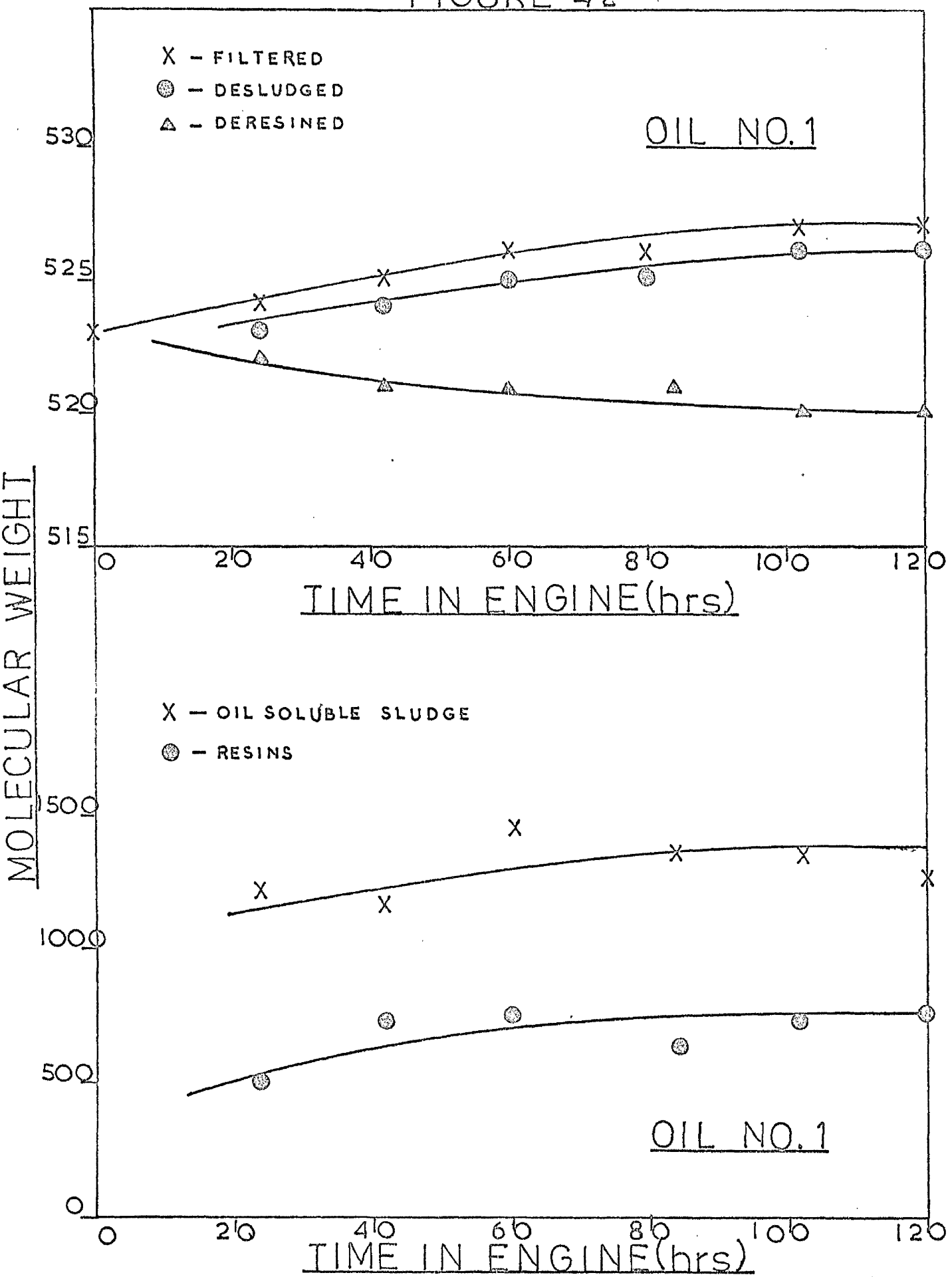

X – FILTERED
– DESLUDGED
△ – DERESINED
OIL NO. 1
530
525
520
515
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
MOLECULAR WEIGHT
X – OIL SOLUBLE SLUDGE
– RESINS
1500
1000
500
0
OIL NO. 1
TIME IN ENGINE(hrs)

FIGURE 43

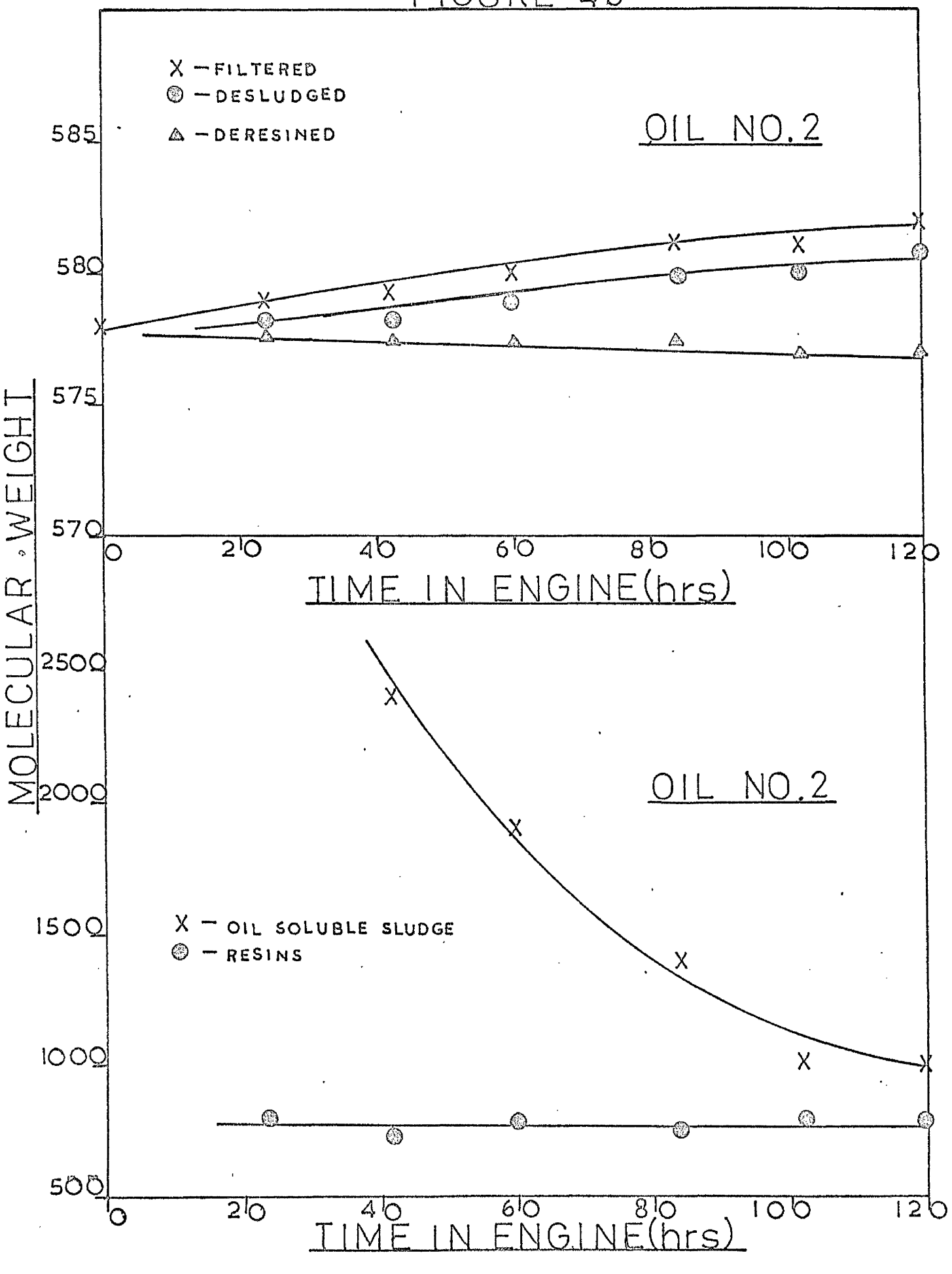

X — FILTERED
◎ — DESLUDGED
△ — DERESINED
OIL NO. 2
585
580
575
570
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
MOLECULAR WEIGHT
2500
2000
1500
1000
500
X — OIL SOLUBLE SLUDGE
◎ — RESINS
OIL NO. 2
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 44

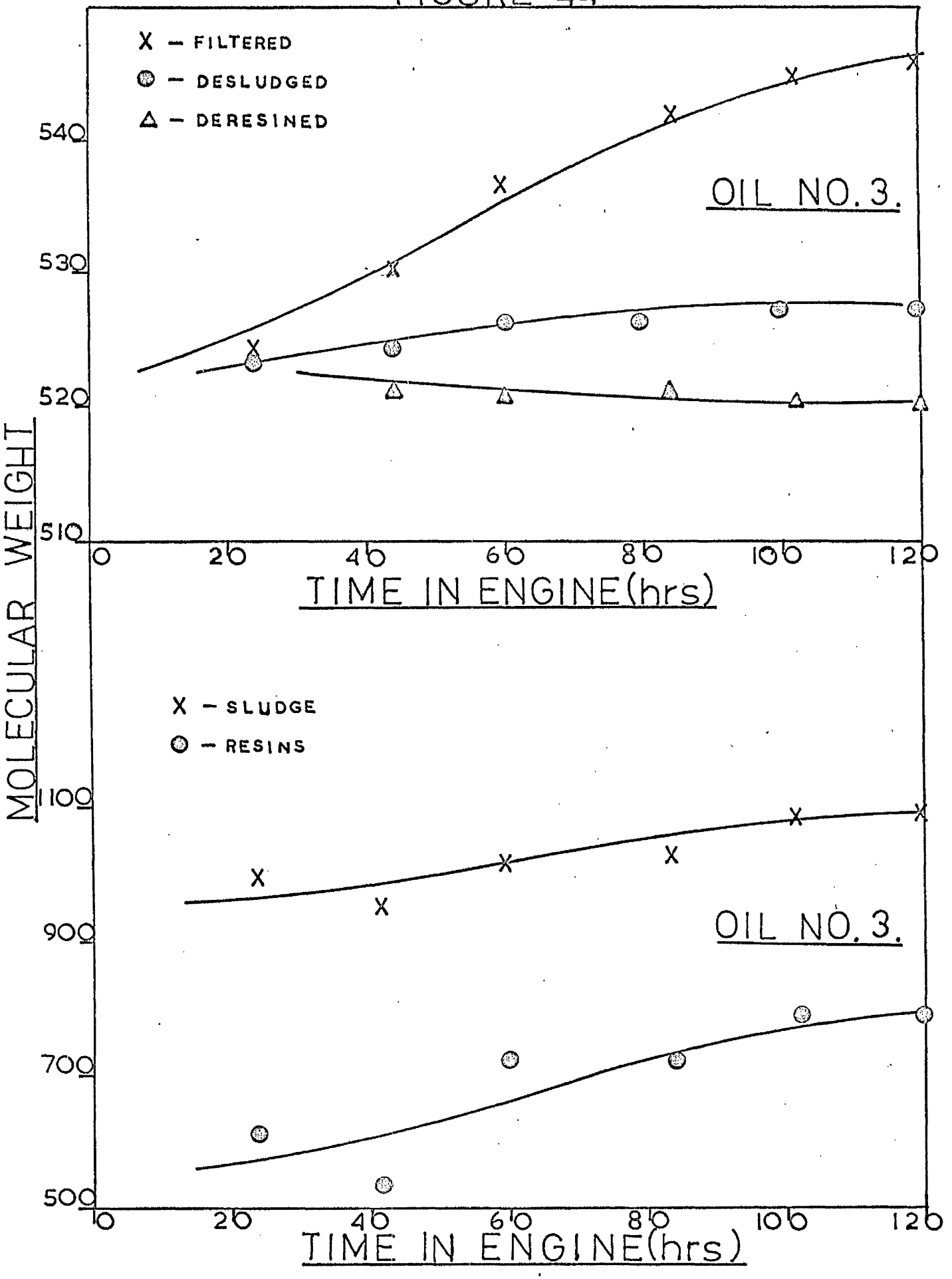
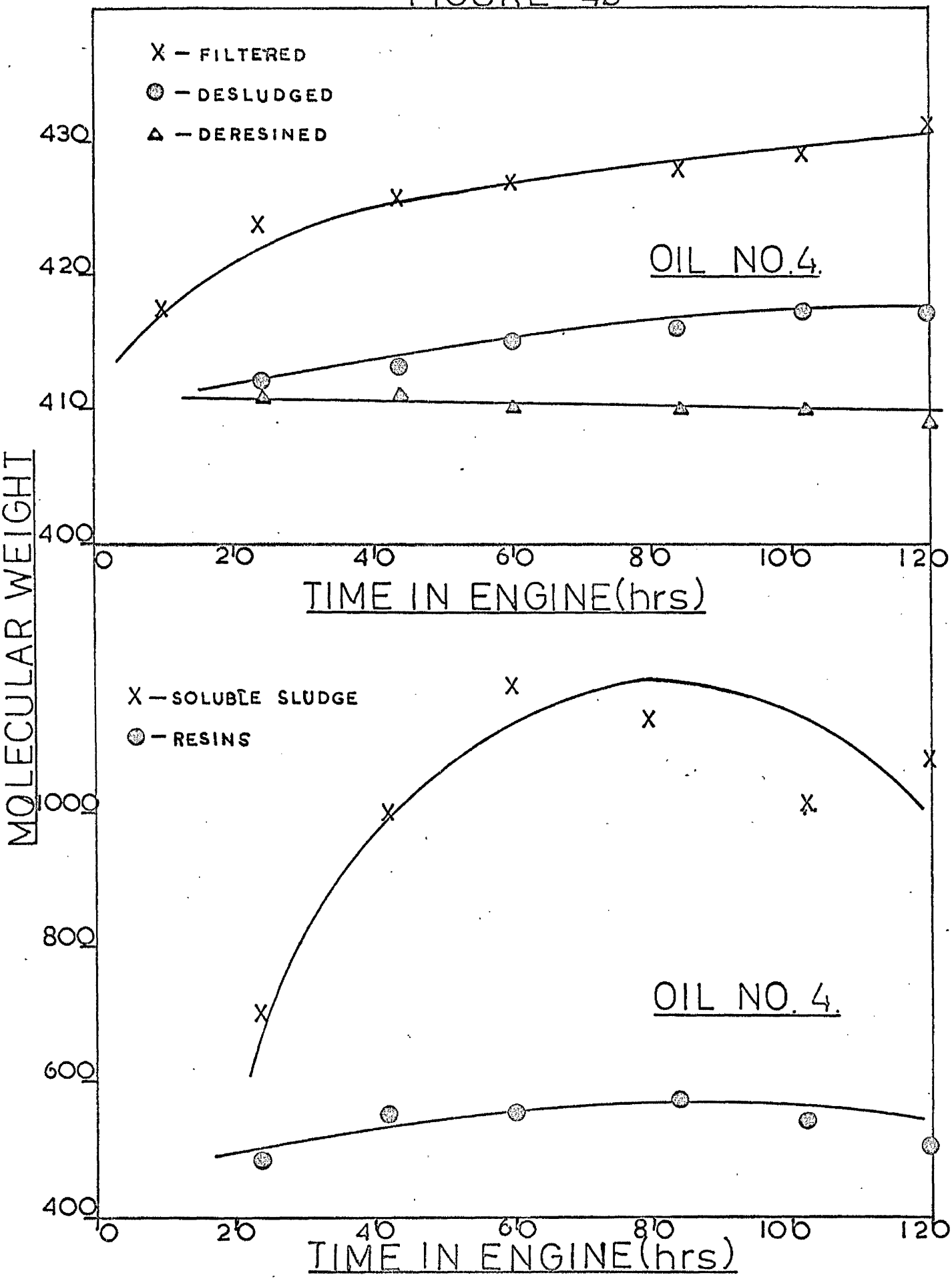

X — FILTERED
◉ — DESLUDGED
△ — DERESINED
OIL NO. 3.
MOLECULAR WEIGHT
540
530
520
510
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
X — SLUDGE
◉ — RESINS
OIL NO. 3.
1100
900
700
500
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 45


X — FILTERED
◎ — DESLUDGED
△ — DERESINED
OIL NO.4.
MOLECULAR WEIGHT
430
420
410
400
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)
X — SOLUBLE SLUDGE
◎ — RESINS
OIL NO. 4.
1000
800
600
400
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

as the time in the engine increased. The molecular weights of the oil soluble sludges had values which indicated that dimerisation had taken place during their formation, whereas those of the resins were only slightly greater than those of the original oils. Thus, it would appear that soluble sludge is formed by oxidative polymerisation of resins, and that resins are formed by the comparitively slight oxidation of the lubricating oil molecules.

7. Properties of the Recovered Oils

After removal of the resins from the deteriorated samples the properties of the recovered oils were essentially the same as those of the original oils. This effect was also noticed when the oils were air-oxidised and then deresined.

The densities of the deresined oils tended to be slightly lower than the original oils, with all four oils showing about the same decrease from the densities of the undeteriorated oils.

Molecular weights tended to be almost the same as those of the original oils, but in all four cases showing a slight decrease. When these oils were oxidised in the I.P. test a great deal of fluctuation in the molecular weights of the recovered oils was observed. The recovered oils from the engine show no such variation. The fact that the molecular weight of the resins does tend to decrease shows that the heavier hydrocarbons are being attacked as before.

The acidities of the deresined oils were found to be the same as those of the undeteriorated oils, or slightly less. However, the acid numbers of the deresined oils from the engine samples were very much lower than those of the deteriorated oils.

Deresined oil viscosity of all four oils used in the engine was lower than that of the original oil and in all cases tended to decrease as time spent in the engine increased. This compared well with the viscosity changes observed when the I.P. oxidised oils were deresined by fuller's earth treatment.

Once again it is apparent that the material which suffered the greatest attack during oxidation was that which contributed most to the density, viscosity and molecular weight of the original oils. When the four oils were oxidised in the I.P. test the molecules which were attacked in Oils number 1 and 2 seemed to be of a more uniform nature than those of Oil number 4, but it does not appear possible to draw the same conclusion in this case, although the trend was towards this being so.

8. Structure of the Recovered Oils

The carbon distribution in the recovered oils, as determined by the Waterman Ring Analysis, is shown in figures 46,47,48 and 49.

In all four instances the percentage paraffinic material in the oil molecule, after 120 hours deterioration, showed an increase. The biggest change in C_P was seen in the deresined samples of Oil number 4.

The percentage naphthenic C_N material in the recovered oils showed an increase in Oils 1,3 and 4 but a decrease in the case of Oil number 2. An overall increase in the percentage naphthenic materials in Oils 1 and 4 were observed when oxidised in the modified I.P. test, as was the decrease in C_N of the recovered oils from Oil number 2. Here, Oils 1 and 3 showed only a slight increase in C_N, whereas Oil number 4 showed quite a large increase.

FIGURE 46

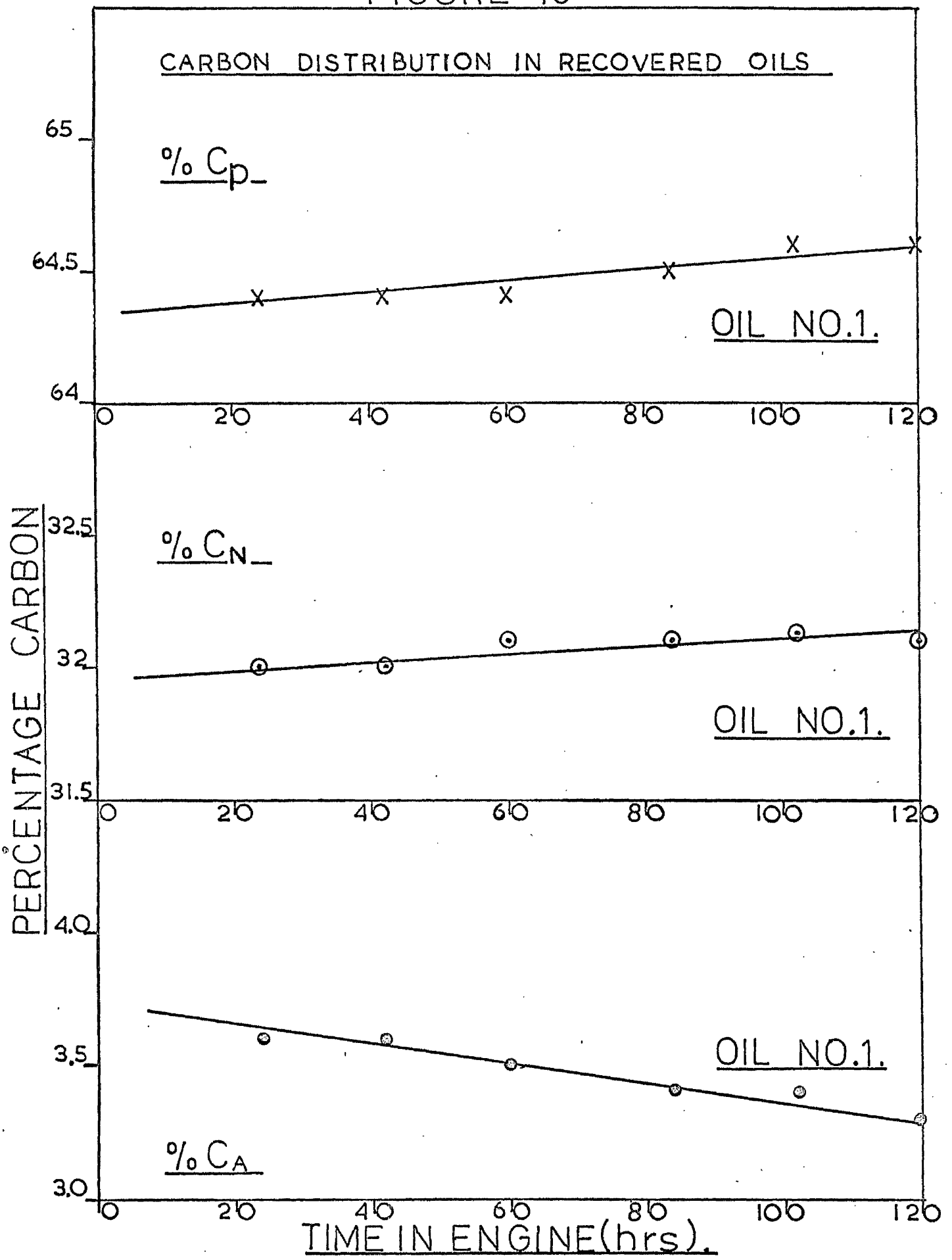

CARBON DISTRIBUTION IN RECOVERED OILS
PERCENTAGE CARBON
% Cp
65
64.5
64
OIL NO.1.
% CN
32.5
32
31.5
OIL NO.1.
% CA
4.0
3.5
3.0
OIL NO.1.
0
20
40
60
80
100
120
TIME IN ENGINE(hrs).

FIGURE 47

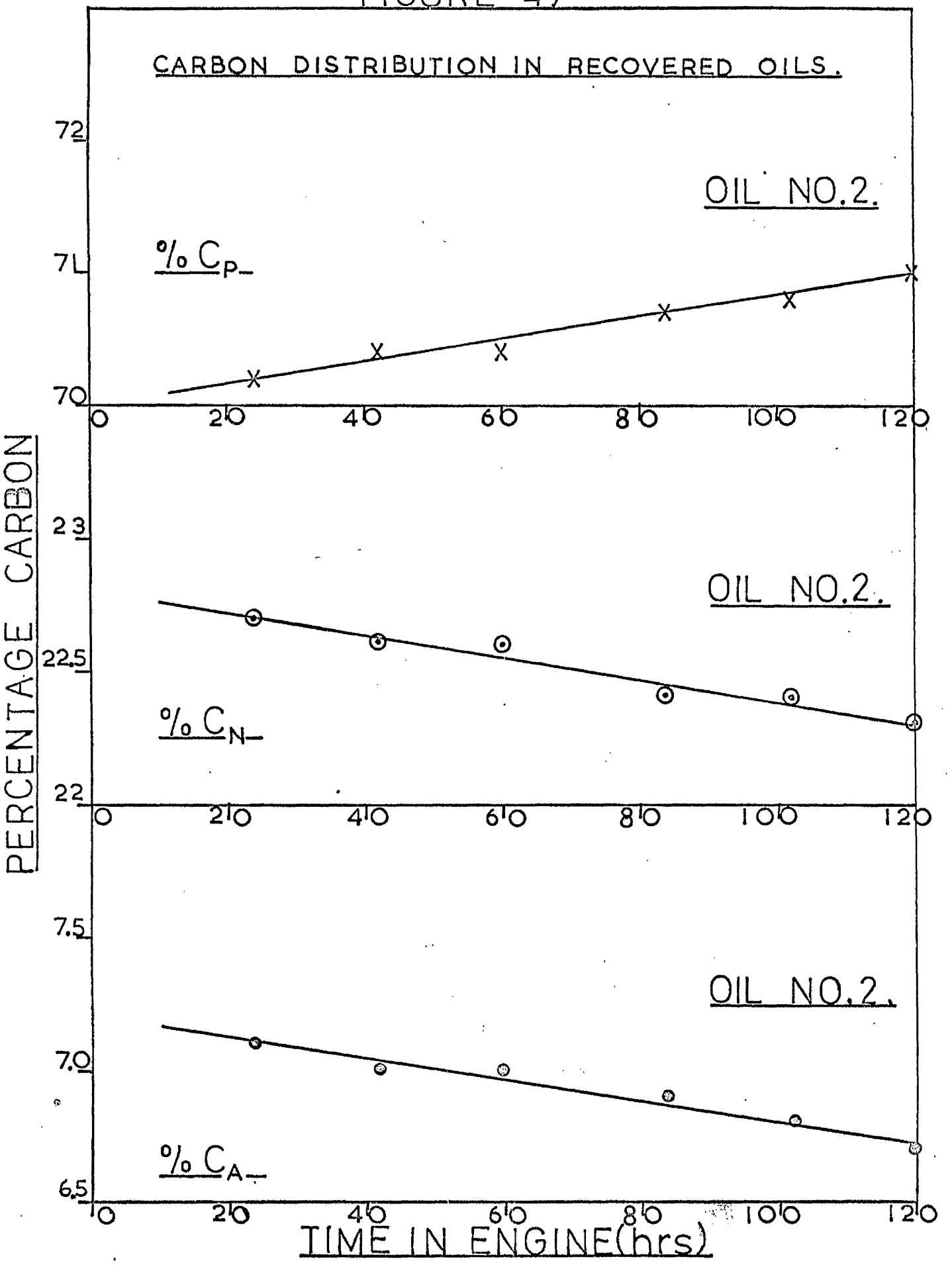

CARBON DISTRIBUTION IN RECOVERED OILS.
PERCENTAGE CARBON
72
71
70
OIL NO.2.
% C_P
0
20
40
60
80
100
120
23
22.5
22
OIL NO.2.
% C_N
0
20
40
60
80
100
120
7.5
7.0
6.5
OIL NO.2.
% C_A
0
20
40
60
80
100
120
TIME IN ENGINE(hrs)

FIGURE 48

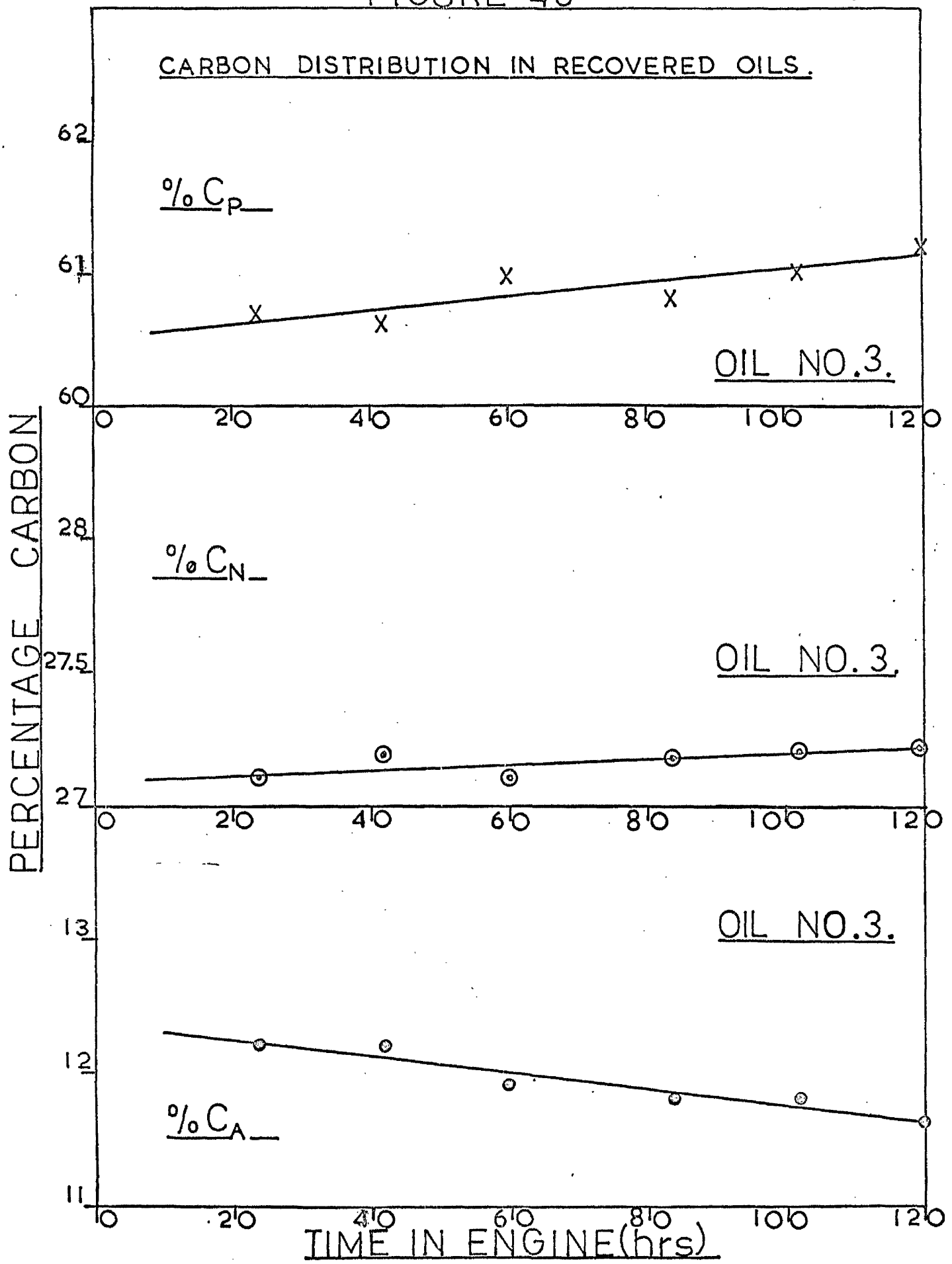
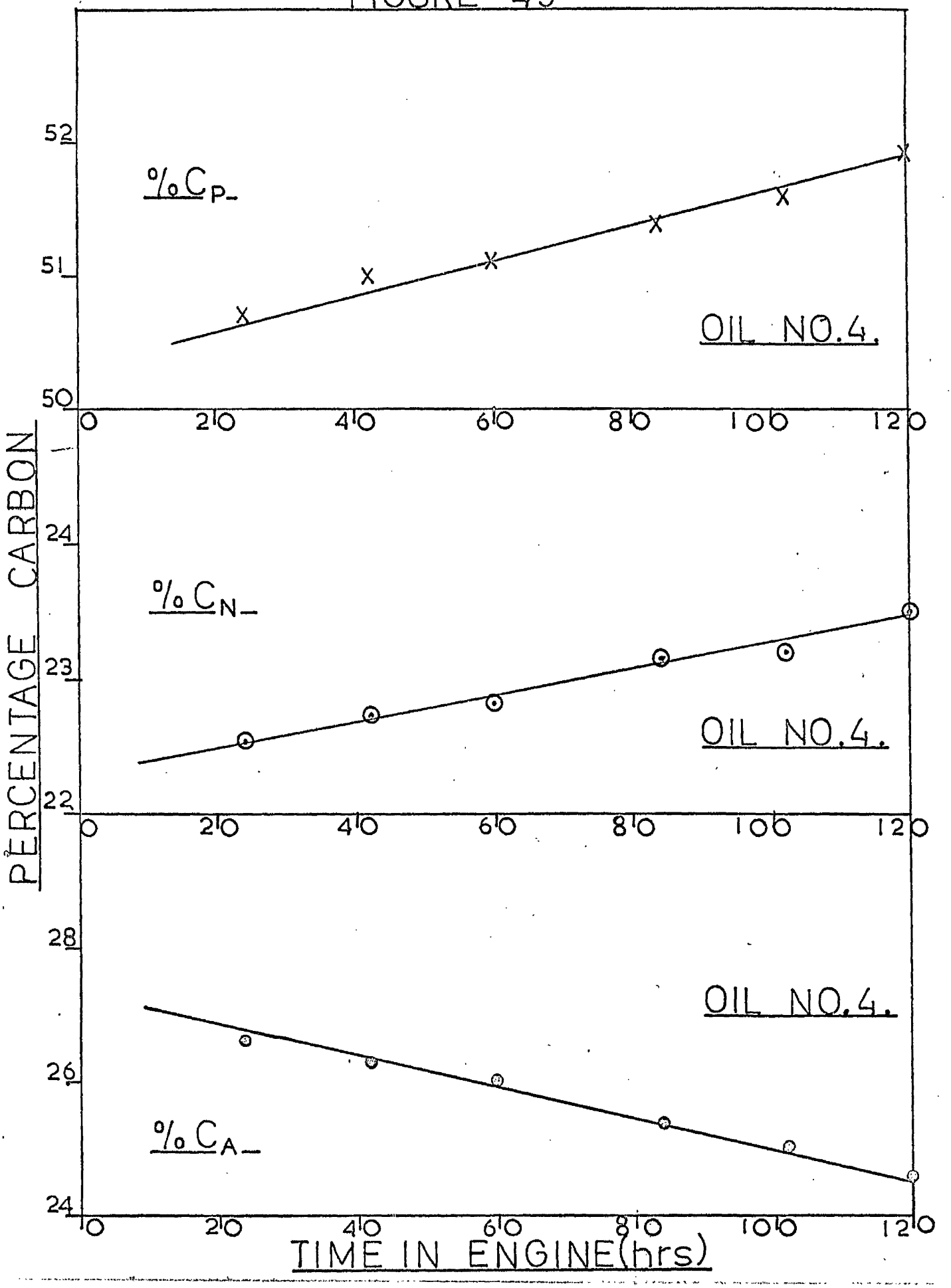

CARBON DISTRIBUTION IN RECOVERED OILS.
62
61
60
% C_P
OIL NO.3.
0
20
40
60
80
100
120
28
27.5
27
% C_N
OIL NO.3.
13
12
11
% C_A
OIL NO.3.
PERCENTAGE CARBON
TIME IN ENGINE(hrs)

FIGURE 49


52
51
50
%Cp
OIL NO.4.
0
2'0
4'0
6'0
8'0
10'0
12'0
PERCENTAGE CARBON
24
23
22
%CN
OIL NO.4.
28
26
24
%CA
OIL NO.4.
TIME IN ENGINE(hrs)

Deresined samples from all four oils showed a large drop in aromatic content after use in the engine, indicating that the aromatic hydrocarbons are the main points of oxidative deterioration in the engine as well as in the I.P. test. Oil number 4, the oil which gave the greatest amount of retained deterioration products, also had the greatest amount of retained deterioration products, also had the greatest change in aromatic content (G_A).

CHAPTER XI

CHAPTER XI

Oxidative - Deterioration of Lubricating Oils

Analysis of used I.C. engine crankcase oils, taken from engines run on the road and in the laboratory, has shown that the oil-insoluble phase consists of the combustion chamber smoke particles, wear particles, and material drived from the oil by oxidation (116). The chloroform - soluble fraction of the oil-insolubles gives a measure of the contribution of oil oxidation to the insoluble phase, since chloroform - insolubles are considered to have originated as part of the engine and from the blow-by of combustion gases, and are not considered as being products of the oxidation of the oil. The amount of chloroform - insolubles formed was more likely to be related to the time spent in the engine, to theacidity produced in the oil, and to the increase in viscosity of the oil rather than directly to the oxidation characteristics of the crankcase oil.

Although the effect was not so obvious as in oxidation by the I.P. test, the results from the Pelapone tests indicated that an optimum aromaticity effect was in operation. The less refined oils, i.e. oils with highest aromatic contents, were deteriorated much more than the more refined oils, but Oil number 2 gave fewest retained oxidation products even though it contained more aromatics than Oil number 1.

Even though the deterioration time was up to five times greater than the oxidation time under I.P. test conditions, none of the oils examined gave the same amount of deterioration products as they did in the I.P. test. In the engine Oil number 2 gave a small amount of soluble sludge which it did not give under the more severe conditions of the I.P. test. Oil number 4, on the other hand, gave oil-insoluble sludge in the I.P. test but did not do so in the

Pelapone engine. The operating condition of the engine appears to have encouraged the formation of oil-soluble sludge but not the formation of oil-insoluble sludge. These findings are in accordance with the work of Matthews (116) who found that only lightly refined oils under high temperature and good combustion conditions does oil oxidation directly produce an oil-insoluble phase. It would appear that the main factor controlling the amount and composition of insolubles found in an I.C. engine was the efficiency of the combustion process.

Under the conditions in the engine all four oils gave similar quantities of resins, whereas Oil number 2 gave the greatest amount of resins when oxidised in the I.P. test. The fact that Oil number 2 did not, in this instance, produce more resins than the other oils may be due to the formation soluble sludge at the expense of the resins. This would be in accordance with the data obtained in the I.P. oxidation test which indicated that resins were further oxidised to form soluble sludge.

As in the I.P. oxidation tests an optimum effect, with respect to the relative amounts of aromatics and naphthenic materials, seems to be force regarding the total amount of oxidation products formed by each oil. However, in the case of the Pelapone engine it would appear that the operating conditions of the engine and the presence of metallic catalysts offset, to some extent at least, the formation of naphthenic oxidation inhibitors. Since Oil number 2 gave the smallest amount of retained deterioration products, and was also the only oil which lost naphthenic materials in the deterioration process, it would still appear to be true that naphthenic materials are used in the formation of oxidation inhibitors.

The aromatic contents of the deresined samples from all four

engine-deteriorated oils decreased with time, but in the I.P. test Oil number 2 (the least oxidised) showed a constant aromatic content. In the engine Oil number 2 gave soluble sludge but did not do so when air-blown and indicates that, here also, aromatics are used in the formation of oil-soluble sludge.

The acid numbers of the unfiltered samples, i.e. before chloroform insolubles have been removed, are higher than those samples containing only soluble sludge and resins. The acidity of the chloroform insolubles was probably due to acidic material, formed during the combustion of the unleaded fuel, finding its way past the piston rings into the crankcase.

None of the filtered oil samples from the engine showed the same degree of acidity as they did when oxidised in the I.P. test, as one would expect since fewer oxidation products were formed. Desludging the oils by n-pentane treatment reduced the acidity by an amount which was proportional to the amount of oil-soluble sludge formed. When resins were removed the acidity fell to almost the same value as that of the original oil. Thus, it would appear that the formation of acidic materials in the engine followed the same process as it did in the I.P. test, i.e. there was a transfer of acidity components from resins to sludges.

The desludged oils derived from the engine deteriorated samples did not show a similar linear raltionship between paraffinic content and acidity as did the desludged oils from the I.P. test. Obviously, the formation of acidic resins in the Pelapone I.C. engine was not only associated with the paraffinic content of the oil.

The increase in oil viscosity as deterioration time increased was again dependant on the total amount of retained oxidation products present, with the bulk of the increase being due to the resins and not to the sludges as

in the I.P. test. However, when the viscosity increase was considered in the light of the relative amounts of oil-soluble sludge and resins formed, it became obvious that soluble sludge gave the greater viscosity increase per gramme of oxidation product.

The samples containing chloroform insolubles gave viscosities which were very little greater than those of the filtered oils, and in the case of Oil number 2 no difference could be detected between the viscosity of the filtered samples and those containing chloroform insolubles. Once again, when the relative weights of the two types of insolubles were considered, it was found that per gramme of chloroform insoluble the degree of viscosity increase was similar to that given per gramme of oil-soluble sludge. Deresined oil samples from the I.P. oxidation tests had viscosities lower than those of the original oils and the same effect was observed when the engine deteriorated oils were deresined.

Although the increase was not so great as in the I.P. oxidised oils, the samples of all four oils taken from the crankcase showed distinct increases in density which depended upon the amount of soluble sludge and resins formed. The work done on the I.P. oxidised samples showed that there was a linear relationship between the total number of rings per mean molecule and the increase in density. A similar dependance on the total number of rings per mean molecule was apparent in the density increases observed in the engine deteriorated oils.

In general, the properties of the various retained oxidation products in the engine were similar to those formed in the I.P. test, both oil-soluble sludge and resins having higher density values than the original oils.. Removal of oil-soluble sludge reduced the oil density in proportion to the

amount of sludge formed after any given time, and the densities of these oils were reduced to values below that of the original oils and it would seem to be the case that sludges and resins were formed by oxidative-deterioration of the heavier hydrocarbon molecules present in the original oils. It was also observed that sludges were more dense than resins and that both oxidation products had similar values of density as the corresponding products formed in the I.P. test.

It was apparent that deterioration in the Pelapone engine also gave oil-soluble sludge which was more acidic than the resins, but that the acid numbers of the sludges and resins were lower than those of the sludges and resins formed by air-blowing at high temperature.

The resins formed under engine conditions had molecular weights only a little greater than those of the original oils, indicating that, as in the I.P. tests, the resins were formed by addition of oxygen to the oil molecule. Oil-soluble sludges, however, had molecular weights which were much greater than those of the original oils and of the resins. The molecular weights of the soluble sludge were such as to suggest that their formation was due to the uniting of two oil molecules during the deterioration reaction. Thus, even in the different conditions of the engine, it would appear that oxidative-polymerisation was the reaction which was responsible for the formation of oil-soluble sludge, whilst resin formation was due to a comparatively light oxidative attack on the oil molecule.

From the foregoing evidence it would appear that, in an I.C. engine also, aromatics are oxidised to oil-soluble sludge since all four oils showed an increase in the paraffinic content of their deresined samples and decrease in their aromatic contents. This is further emphasised by the fact that Oil

number 2 gave an oil-soluble sludge and a decrease in aromaticity when used in the engine, but showed neither of these effects when oxidised in the I.P. test.

The deresined samples from Oil number 2 showed a similar decrease in naphthenic content in both methods of deterioration, indicating that in both cases naphthenes formed oxidation products which inhibited oxidation in the I.P. test but did not apparently do so in the engine. However, Oil number 2 gave the smallest amount of oil-soluble sludge and the effect of the oxidation inhibitors formed by naphthenic materials may still be in operation but offset to some extent by the presence of metallic catalysts.

The engine operating conditions favoured the formation of resins and oil-soluble sludge but did not favour the formation of oil-insoluble sludge. Apart from Oil number 2, all the oils gave relatively more resins than soluble sludge in the engine than they did in the I.P. oxidation test. Thus, there seems to be a sufficient supply of oxygen to aid the formation of resins and oil-soluble sludge but not enough for the further oxidation of oil-soluble sludge to insoluble sludge. Because Oil number 2 formed oil-soluble sludge in the engine it may be supposed that the presence of metals encourages the oxidative-polymerisation of resins to soluble sludge, but it is more likely to be the case that the oxidation inhibitors formed by the naphthenic materials reacted with these metals and their powers of inhibition were diminished.

The components of the original oils which were attacked in the engine were those which contributed most to the viscosity, density, and molecular weight of the oils. Less refined oils are generally composed of a wider variety of hydrocarbon types than the more refined oils, and it was shown in the I.P. test that Oil number 4 was not composed of a uniform series of hydrocarbons. In the

I.C. engine, however, this difference in the compositions of the four oils was not evident. This may have been due to the fact that oil number 4 formed no oil-insoluble sludge in the engine and fewer hydrocarbons would take part in the deterioration reactions.

Even under the engine running conditions it still seemed to be true that the hydrocarbons present in the lubricating oils were first oxidised to resins which were further oxidised to oil-soluble sludge. This soluble sludge had a higher molecular weight, density, and acidity than the resins, which was possibly due to the formation of oil-soluble sludge from resins by an oxidative - polymerisation reaction similar to that put forward to explain the results of the I.P. test.

However, it would appear that equilibrium had not yet been reached in the formation of oil-soluble sludge from resins since the density of oil-soluble sludge varied a good deal while the density of the resins were only just tending towards a more constant value. Also, the acid numbers of the sludge had not reached constant value while those of the resins had.

It would therefore be of interest to continue the running of the Pelapone I.C. engine until equilibrium is reached. When this has been achieved it may then be possible to determine whether or not oil-insoluble sludge then commences to be formed from the oil-soluble sludge.

APPENDIX

APPENDIX

I. SLUDGE DETERMINATION

Oil insoluble materials of hydrocarbon origin which result from the oxidation of the oil are known as "sludges". This definition takes no account of other degradation, polymerisation or oxidation products which may be dissolved in the oil. This second class of material may be considered as "soluble sludges", since they are the products of the oxidation and were not present originally. Soluble sludge may be potential insoluble sludge and hence is just as objectionable as insoluble sludge.

Levin and Towne (117) described a method of determining sludge values and a modified version of their method was used in the present work. The method employed consisted of the direct determination of soluble sludge and the indirect determination of insoluble sludge since the direct determination of insoluble sludge gives rise to difficulties in the solvent treatment of the sludge to remove all traces of oil. Most hydrocarbon solvents either dissolve the whole or part of the sludge or precipitate soluble sludge from the remaining oil.

Sludge and asphaltic materials are relatively insoluble in paraffin solvents, the lower the boiling point of the paraffin the more insoluble the sludge. Levin and Towne used a pentane mixture for precipitation of the sludge, since experiments showed that it did not dissolve material originally undissolved in the oil itself.

"Oil soluble sludge" may be defined as that portion of a filtered oil which is insoluble in pentane. Liquid propane has also been used (118) but is less desirable than pentane since it tends to precipitate material normally present in the unoxidised oil.

PROCEDURE

In the determination of sludge values a well stirred sample of the oxidised oil was filtered as quickly as possible through a Gooch crucible, packed with asbestos and heated to 75°C. by means of a heating tape. Two samples were thus obtained - a clarified sample and an unclarified sample - and sludge values were determined for both.

A 10g. sample was weighed into an Erlemeyer flask and 100ml. pentane added. The flask was then shaken and allowed to stand for at least 12 hours. The solution was then filtered through an asbestos packed Gooch crucible which was washed with pentane and dried in an oven at 110°C. for one hour. From the difference in weights of the pentane insoluble matter found in the clarified and unclarified samples the insoluble sludge was calculated using the following relationship:

$$C = A - B \cdot \frac{10-A}{10-B}$$

where A = sludge not dissolved in pentane, original oxidised oil sample (g./10g.);

B = sludge not dissolved in pentane, filtered sample (g./10g.);

and C = oil insoluble sludge (wt.%).

From this equation it follows that 10 A gives "total sludge" (wt.%) 10 B gives oil soluble sludge (wt.%) and C gives oil insoluble sludge (wt.%).

The filtrates from the two samples were heated to 60°C. under reduced pressure to remove all the pentane solvent, and the "desludged" oil kept for further analysis.

II. CHLOROFORM INSOLUBLES

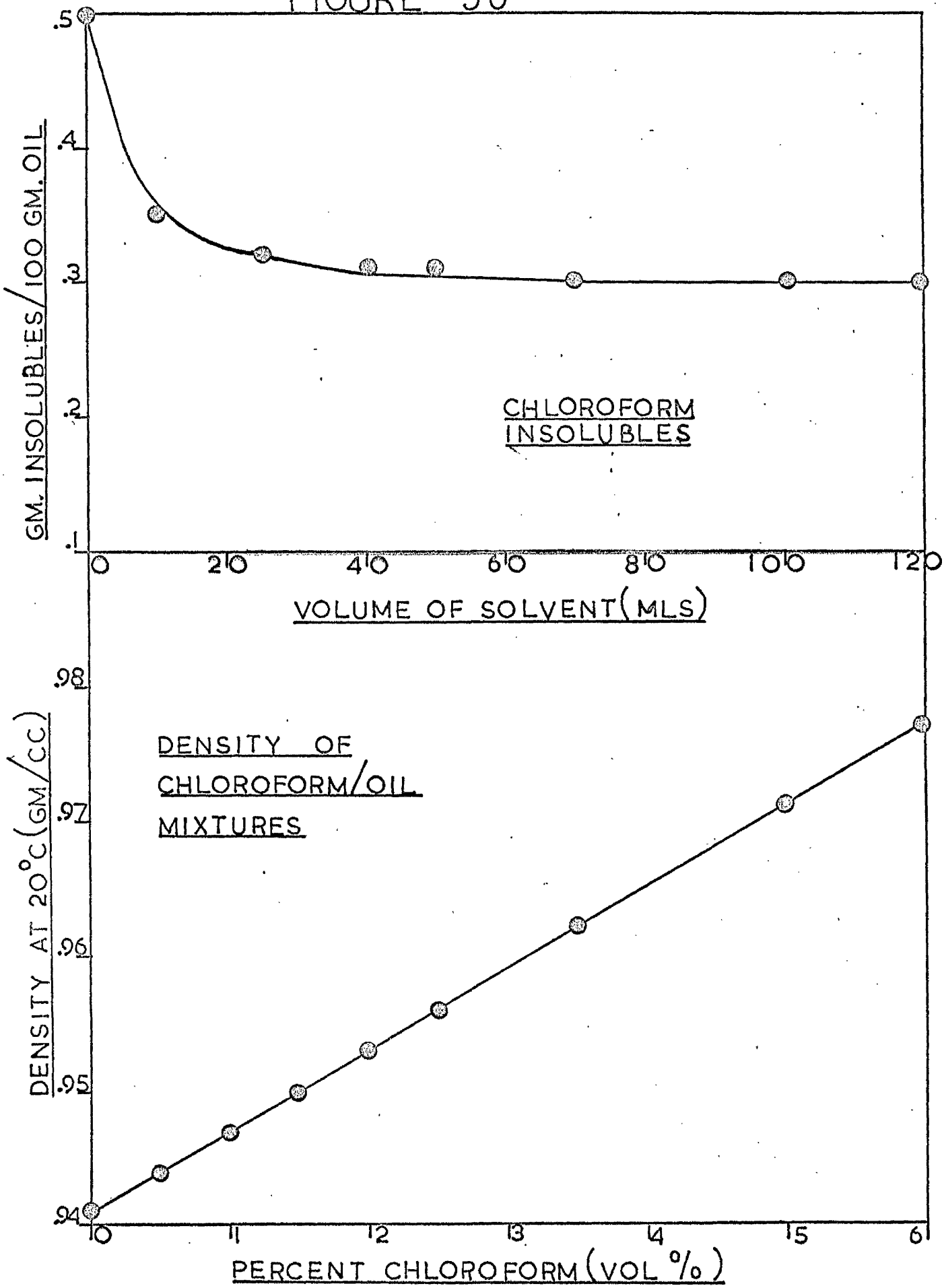
When oils are oxidised in an I.C. engine, a fourth type of product is obtained - chloroform insolubles, which are comprised of material from the wear of engine parts and blow - by of combusted material. This extreneous material is insoluble in chloroform unlike the insoluble and soluble sludges and resins mentioned earlier. Although it had been well established that this insoluble material could be separated from the oil by treating with chloroform and filtering, it was necessary to carry out a series of experiments to determine the amount of chloroform to add per gramme of oil, the contact time required, and the most efficient method of removing the chloroform from the filtered mixture.

a) Quantity of Chloroform used:

Preliminary experiments showed that the oil sludges dissolved rapidly in chloroform as long as fairly frequent shaking was employed. For the purpose of this work it was decided to give the oil samples a contact time of at least 12 hours to ensure that all the chloroform soluble sludge would dissolve. Therefore, after the addition of chloroform to the weighed oil sample, the flask was shaken at 15 minute intervals for the first two hours and then allowed to stand overnight.

Several 10g. samples of Oil number 4, which had been deteriorated in an I.C. engine, were weighed accurately into 250ml. stoppered flasks and various quantities of chloroform were added ranging from 10ml. to 200ml. The flasks were then shaken as before and left overnight in a dark cupboard at room temperature.

FIGURE 50


.5
.4
.3
.2
.1
GM. INSOLUBLES/100 GM. OIL
CHLOROFORM INSOLUBLES
0
20
40
60
80
100
120
VOLUME OF SOLVENT (MLS)
.98
.97
.96
.95
.94
DENSITY AT 20°C (GM/CC)
DENSITY OF CHLOROFORM/OIL MIXTURES
10
11
12
13
14
15
16
PERCENT CHLOROFORM (VOL %)

Each sample was then filtered through an accurately weighed Gooch crucible packed to about half its depth with asbestos. The filter was then washed with 100-120°C petroleum ether which removed any oil sticking to the filter but did not dissolve the chloroform insoluble material. The Gooch crucible was then dried in a vacuum oven at 29.5" Hg. vacuum and 60°C. When cool the crucible was again weighed accurately and the weight of chloroform insolubles obtained by difference and expressed as a percentage by weight of the original oil sample.

The results of these series of determinations are expressed graphically in fig. 50. From this graph it can be seen that high values are obtained initially, due no doubt to some of the oil-insoluble sludge remaining undissolved in the chloroform. After about 75ml. chloroform/10g. oil had been added constant values were obtained, indicating that all the oil - insoluble sludge had dissolved leaving only the chloroform insoluble material which originated from the engine.

Hence, it was decided to determine the chloroform insolubles by adding chloroform in the ratio of 10ml. : 1g. oil, which would ensure complete solution of the oil - insoluble sludge and would also reduce to almost negligible proportions any losses due to spillage.

b) Removal of solvent:

The solvent in this case is chloroform which had a b.p. of 61.26°C, at atmospheric pressure, a density of 1.489g./c.c. at 20°C., a refractive index of 1.4464 at 20°C., a viscosity of 0.58 c.p. at 20°C., and a molecular weight of 119.39. Obviously if any of this solvent remains in the chloroform insoluble free oil any measurements of density, refractive index, viscosity, molecular weight, etc. on these samples will be affected. This may lead to erroneous

results in any n-d-M analyses which may be carried out. Hence it is desirable to remove all traces of chloroform from the samples.

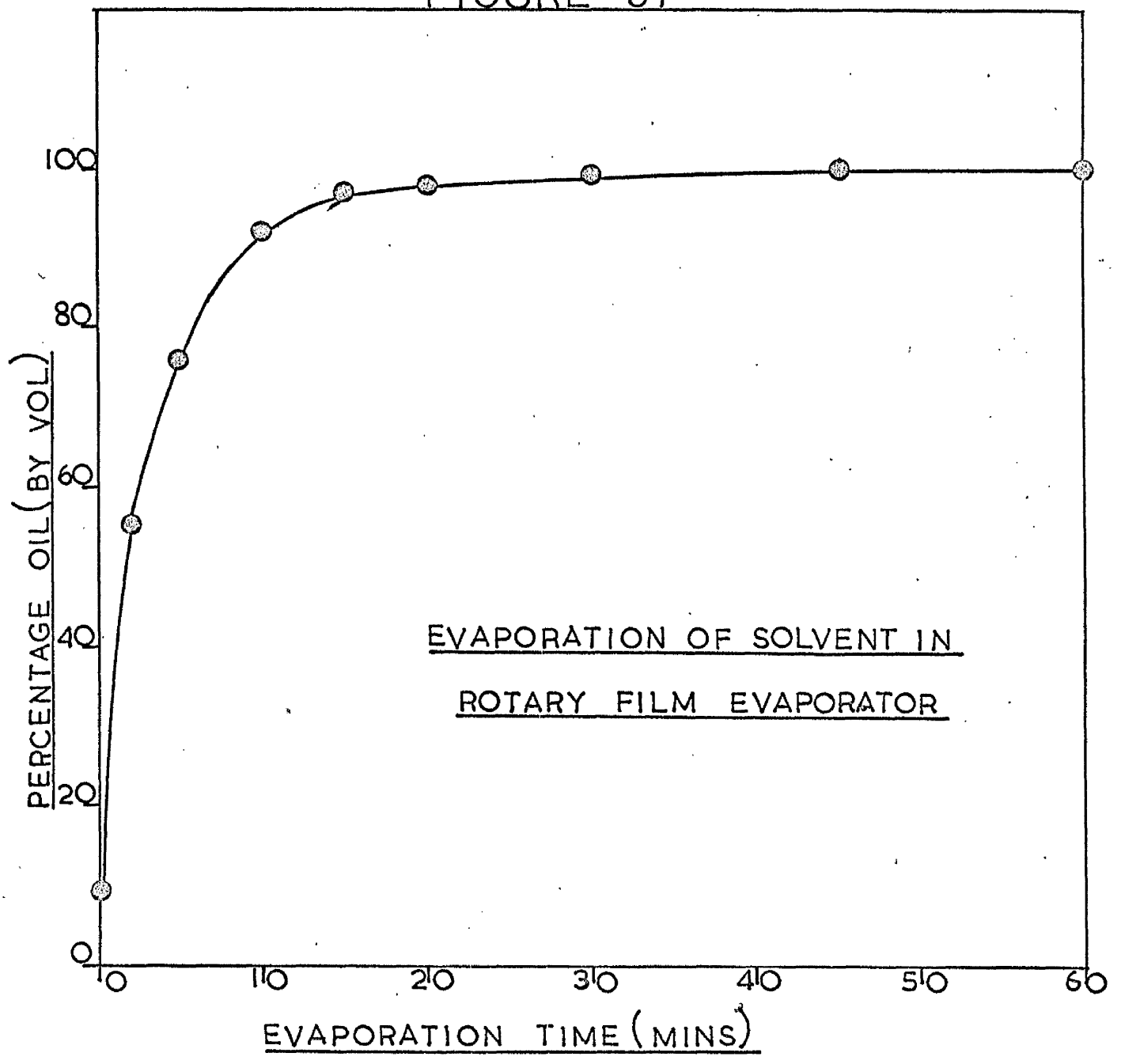
Since a rotary film evaporator was used to remove 100°C./120°C. petroleum ether from oil samples it was thought advisable to use the same apparatus to remove chloroform also. This was achieved by heating the evaporator in an oil bath at 100°C. and under 28" Hg. vacuum.

In order to determine the length of time required for complete removal of the solvent, several 10g. samples of Oil number 4 (density 0.9408) were taken and varying amounts of chloroform (density 1.489) added. The densities of these mixtures were then measured and when plotted against the percentage chloroform present a straight line was obtained (fig. 50). This made possible the determination of chloroform content of the oil samples after evaporation.

10g. samples of Oil number 4 were then dissolved in 100ml. of chloroform and placed in the rotary film evaporator for various periods of time. Evaporation was carried out at 100°C. and 28" Hg. vacuum and after evaporation of the chloroform the density of the oil/solvent mixture was determined. This was repeated for longer periods of time until almost complete removal of chloroform had been achieved. The percentage oil present was plotted against evaporation time (fig. 51) and it can be seen that almost complete evaporation is obtained after about 45 minutes.

It was hence decided to carry out evaporation in the rotary film evaporator for 1 hour so that the chloroform content was reduced to less than 0.1% by weight.

FIGURE 51


100
80
60
40
20
0
PERCENTAGE OIL (BY VOL)
0
10
20
30
40
50
60
EVAPORATION TIME (MINS)
EVAPORATION OF SOLVENT IN
ROTARY FILM EVAPORATOR

c) Effect of presence of Chloroform:

Any Oil number 4/chloroform mixture containing 0.1% chloroform by weight will have the following characteristics:

$$d_{av.} = 0.9409$$

$$N_{av.} = 1.5278$$

and $$M_{av.} = 409$$

These values were calculated using the following equations:

$$d_{av.} = \frac{w_1 + w_2}{\frac{w_1}{d_1} + \frac{w_2}{d_2}}$$

$$M_{av.} = x_1 M_1 + x_2 M_2$$

Nav is calculated from:

$$R_{1,2} = \frac{N^2_{av.} - 1}{N^2_{av.} + 2} \frac{M_{av.}}{d_{av.}}$$

where $$R_{1,2} = x_1 R_1 + x_2 R_2$$

and $$R_1 = \frac{N_1^2 - 1}{N_2^2 + 2} \frac{M_1}{d_1}$$

In the above equations,

w = respective weights,

x = mole fraction,

and R = molar refraction.

Subscript 1 refers to the oil and 2 refers to the solvent.

The n-d-M analyses of such a mixture and the oil itself are given in the following table:

	Mixture	Oil	Deviation	Recommended Repeatability
$\%C_A$	27.3	27.5	-0.2	0.8
$\%C_R$	50.1	49.8	+0.3	1.6
$\%C_N$	22.8	22.3	+0.5	1.8
$\%C_P$	49.9	50.2	-0.3	1.6
R_A	1.40	1.42	-0.02	0.06
R_T	3.20	3.19	+0.01	0.12
R_N	1.80	1.77	-0.03	0.14

From this table it can be seen that the deviations of the chloroform/oil mixture from the values for the oil itself are well within the limits of repeatability laid down by Van Nes and Van Weston (28).

Therefore evaporation in the manner described is a suitable procedure for the removal of chloroform since this leaves less than 0.1% chloroform by weight which in turn will produce negligible error in any subsequent n-d-M analysis

III. RESIN DETERMINATION

When oil insoluble and oil soluble sludges have been removed from an oil, there still remains oxidised material which cannot be precipitated by hydrocarbon solvents. This material is not oxidised or polymerised to any

great extent and is loosely termed "resins". Because these resins and the more highly oxidised material contain oxygen they are more polar than the hydrocarbons from which they are derived, and hence can be adsorbed on to active clays or earths. The adsorption of resins may not be entirely selective (102), some high molecular weight aromatics being adsorbed as well as resins. On the other hand, a second group of workers (101) maintain that there is a sharp division between the adsorption of resins and aromatic hydrocarbons.

Since there appeared to be some conflict over this question of relative adsorption Beaton (88) carried outwork with a view to adopting fullers' earth as an adsorbent for the quantitative determination of resins. The principles of the determination are therefore those put forward by Matthews (116) and Beaton.

The fullers' earth used for this purpose was produced by the Fullers' Earth Union, England, and is a calcium montmorillonite containing small proportions of other minerals as impurities. There is no definite chemical composition for fullers' earth, $(Al, Fe, Mg)\ Si_8\ O_{20}\ (OH)_4$ representing the main structure with Ca, Mg, Na and H as exchangeable ions. The main physico-chemical properties of fullers' earth are related to the existence of electrical dipoles and double layers in its structure. Adsorption of acidic material from a non-polar solvent is due to formation of hydrogen bonds, the surface atomic structure of fullers' earth being well suited for this purpose.

PROCEDURE

About 20g. of the oxidised oil were accurately weighed into a flask and dissolved in 100°C./120°C. petroleum ether in the ratio of solvent/oil = 25ml./1g. since the removal of the oxidised material from an oil depends upon the quantity of fullers' earth used and the agitation time, a standard agitation time of 15 minutes was employed and the amount of fullers' earth added depended

upon the oxidation time. The longer the oxidation time the greater the quantity of fullers' earth required. Knowing the period of oxidation and the oxygen content the necessary amount of fullers' earth was estimated, added to the solvent - oil mixture and agitated.

After 15 minutes a small sample was filtered and matched, with respect to colour, with a prepared sample of unoxidised oil and solvent since this had been found (88) to be the simplest and quickest way in which to determine whether or not extraction was complete. This was made possible by the fact that the optical density of these solutions depends more on the oxygen content than on the chemical structure, the optical density of an unoxidised oil/solvent mixture being almost the same as that of a fullers' earth treated oil/solvent mixture.

If extraction was not complete further quantities of fullers' earth were added until a filtered sample matched the standard sample. The complete oil/solvent mixture was then filtered, and fresh solvent added to the fullers' earth and the mixture agitated for 15 minutes to remove any traces of unoxidised oil which may have been adsorbed. This mixture was then filtered and the two filtrates combined.

The 100/120°C. petroleum ether solvent was then removed by means of a rotary film evaporator which reduced the petroleum ether content to less than 0.1% by weight. In this type of evaporator a flask is rotated in a liquid paraffin oil bath at 100°C. for 1 hour and under a vacuum of 28" Hg. The bulk of the solvent is removed in the first few minutes, the remaining time being required to remove the final traces.

Rotary film evaporation was the best method for the removal of solvent since it reduced the petroleum ether content to such a low value that it had little or no effect on the subsequent n-d-M analysis.

The recovered oil remaining in the evaporator flask was removed by solution in 30/40°C. petroleum ether and transferring to a weighed sample bottle. Heating to 60°C. under 29.5"Hg. was sufficient to remove the low boiling petroleum ether. The sample bottle and contents were re-weighed and the difference in weight between the original oil and the recovered oil gave the total amount of material oxidised. Knowing the sludge values for a particular oil the amount of resins present can be determined by difference.

The recovered or "deresined oil" was suitable for analysis by the n-d-M method since the oxygen content had been reduced to well below 0.5%.

IV. MOLECULAR WEIGHT

Molecular weights were determined ebullioscopically in preference to the cryoscopic method (28), and were calculated using the following equation for ideal conditions.

$$M = \frac{K.w}{T}$$

where M = molecular weight of solute,

w = weight of solute,

T = elevation in boiling point,

and K = constant whose value is dependant on the apparatus and upon the nature and amount of solvent.

Normally, ideal conditions are never achieved but if small amounts of solute are used the above equation is approximately correct. The value for molecular weight under ideal conditions can be obtained by plotting the apparent molecular weight against the concentration of solute and extrapolating to infinite dilution.

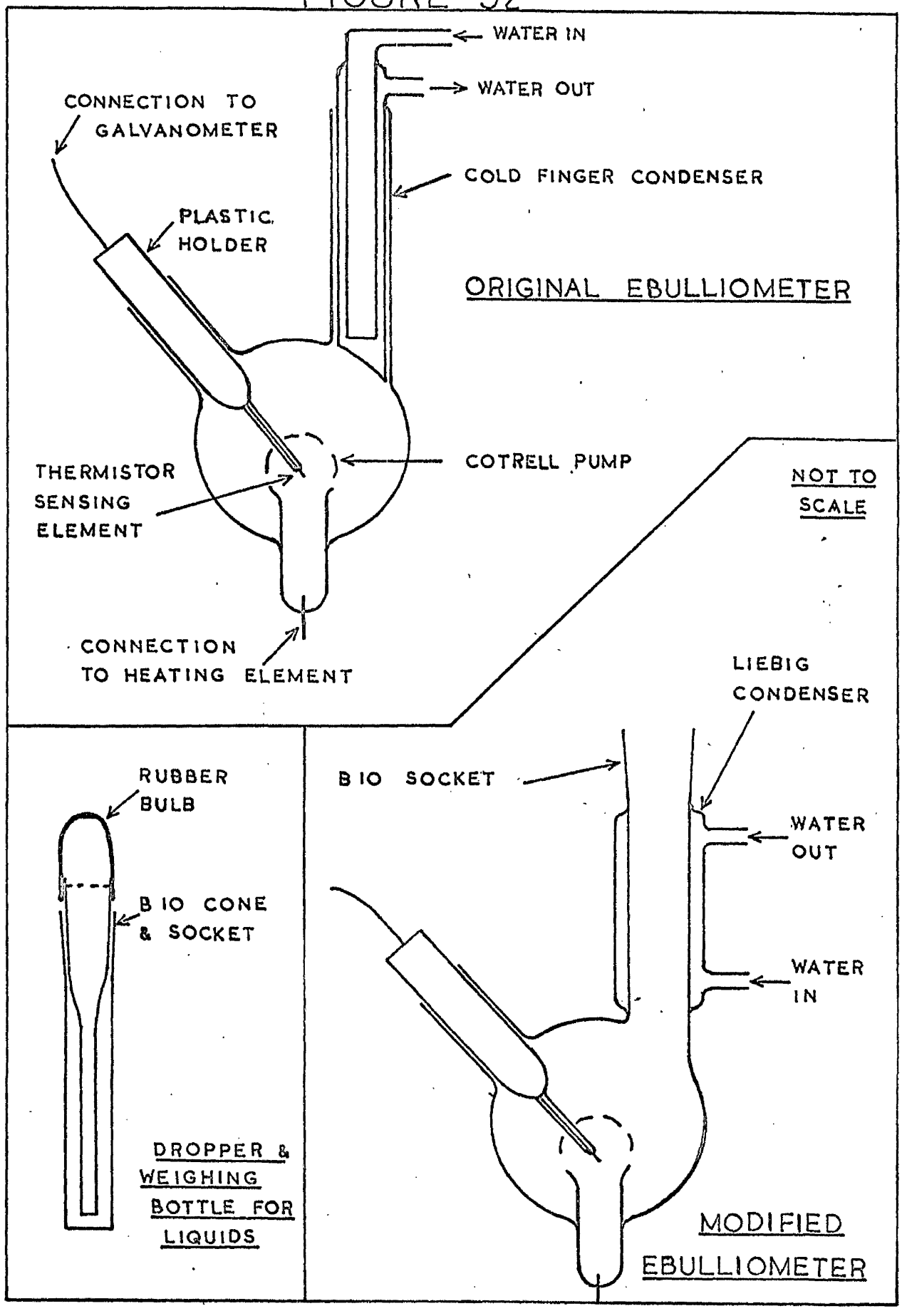
The ebulliometer used was manufactured by Gallenkamp and Co., London and employs a thermistor sensing element in place of a Beckmann thermometer, since a thermistor is of low thermal capacity and responds more quickly to any change in temperature (119). In this instrument, the change in temperature on addition of solute produced a change in the resistance which measured by means of a Wheatstone bridge. The molecular weight of the solute was then calculated from the equation $M = K.\frac{w}{R}$ where R is the change in resistance produced by adding w gm. of solute to the solvent.

The apparatus consisted of an electrical heating block, which heated a modified Cotrell vapour lift pump, surrounded by a draught shield. The ebulliometer body (figure 52) had provision for the insertion of a thermistor sensing element which was connected to a Wheatstone bridge and a galvanometer which indicated any changes in resistance.

When used in its original form (figure 52) the apparatus was operated in the following manner:

After washing with benzene, and drying, exactly 10ml. of benzene at 20°C. were pipetted into the ebulliometer vessel. The control dial of the heating block was set at a predetermined value after assembly of the apparatus

FIGURE 52


WATER IN
WATER OUT
CONNECTION TO GALVANOMETER
COLD FINGER CONDENSER
PLASTIC HOLDER
ORIGINAL EBULLIOMETER
COTRELL PUMP
THERMISTOR SENSING ELEMENT
NOT TO SCALE
CONNECTION TO HEATING ELEMENT
LIEBIG CONDENSER
B 10 SOCKET
WATER OUT
WATER IN
RUBBER BULB
B 10 CONE & SOCKET
DROPPER & WEIGHING BOTTLE FOR LIQUIDS
MODIFIED EBULLIOMETER

and ensuring that there was a steady flow rate of condenser water. When equilibrium had been reached the Wheatstone bridge was balanced and the resistance of boiling benzene noted. In order that solute be added to the benzene the cold finger condenser had first to be removed. When sufficient solute had been added, either in pellet form if solid or from a weighed pipette (figure 52) if liquid, the cold finger condenser was replaced. After stabilisation the new resistance was noted and the process repeated for several solute additions and a constant calculated for each concentration using the formula:

$$K = \frac{R.M.}{w}$$

where K = constant depending upon the apparatus, nature and quantity of solvent;

w = weight of solute added;

M = molecular weight of solute added;

R = resistance change dependant upon the molecular weight and quantity of solute.

The value of K obviously depends upon the concentration of solute and hence it is imperative that no benzene is lost when the cold finger condenser is removed. Each time the condenser was removed the benzene vapour front rose up the receiving arm of the condenser and when it was replaced some of this benzene is trapped between the two glass surfaces. This "hold up" reduced the amount of benzene in the ebulliometer body and hence altered the actual concentration of solute. "Hold up" of benzene in this manner was not constant and varied from addition to addition, and resulted in a marked deviation of values calculated for the constant and molecular weight. Merely averaging these values will entail errors according to Mair (120). A constant "hold up" was therefore required to eliminate these errors.

This was achieved by replacing the cold finger condenser with a permanent condenser jacket round the arm of the ebulliometer vessel. To facilitate the addition of oils to the benzene in the ebulliometer the new Leibig type condenser was fitted with a B.10 "Quickfit" socket and a B.10 cone was extended to form a pipette as shown in figure 52. The results obtained using this modified ebulliometer (figure 53) were much more consistent, and extrapolation to infinite dilution was much more accurate than before.

To correct the ebullioscopic constant for different atmospheric pressures Van Nes and Van Weston (28) gave the formula $K = Ko + 0.24 (Pm-Po)$, where Ko = ebullioscopic constant for the standard hydrocarbon at infinite dilution;

Po = barometric pressure at which Ko is obtained in cm. Hg;

Pm = barometric pressure during the molecular weight determination of oil sample.

Work carried out by Beaton (88) to establish whether or not this equation could be employed with this ebulliometer showed that there was no apparent relationship between the ebulliometer constant and the atmospheric pressure. Further work was therefore carried out, the results of which are expressed graphically in figure 54, which showed that there was some relationship but that there was still too great a spread of results for the values calculated from them to be satisfactory.

Since great care was always taken to add the same amount of benzene at 20°C. it was concluded that the factor causing these deviations was most likely to be moisture. In order to ascertain just what effect moisture did have on the calculation of molecular weight, determinations were carried out using benzene samples which ranged from "dry" (re-distillation and sodium wire) to 'water - saturated".

FIGURE 53

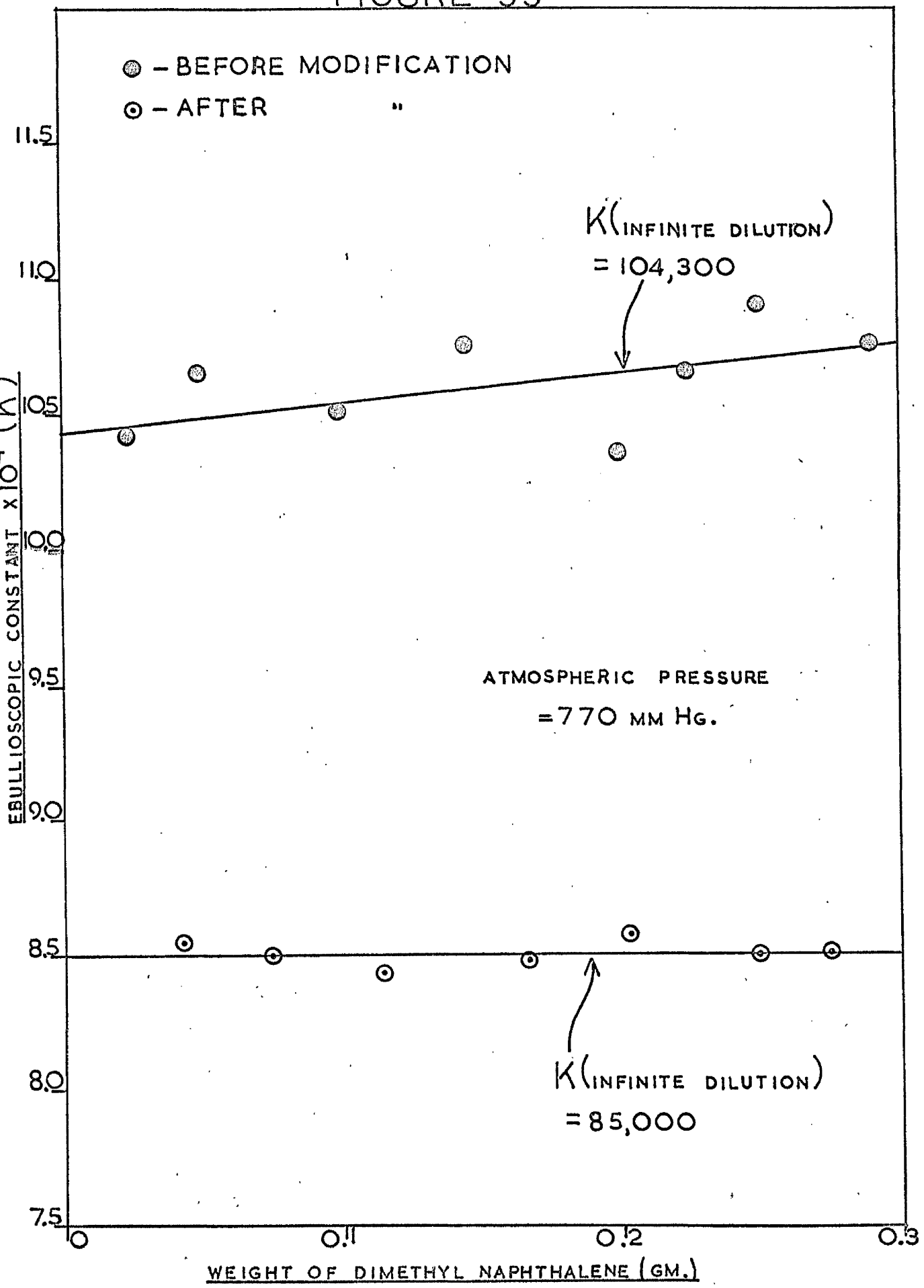
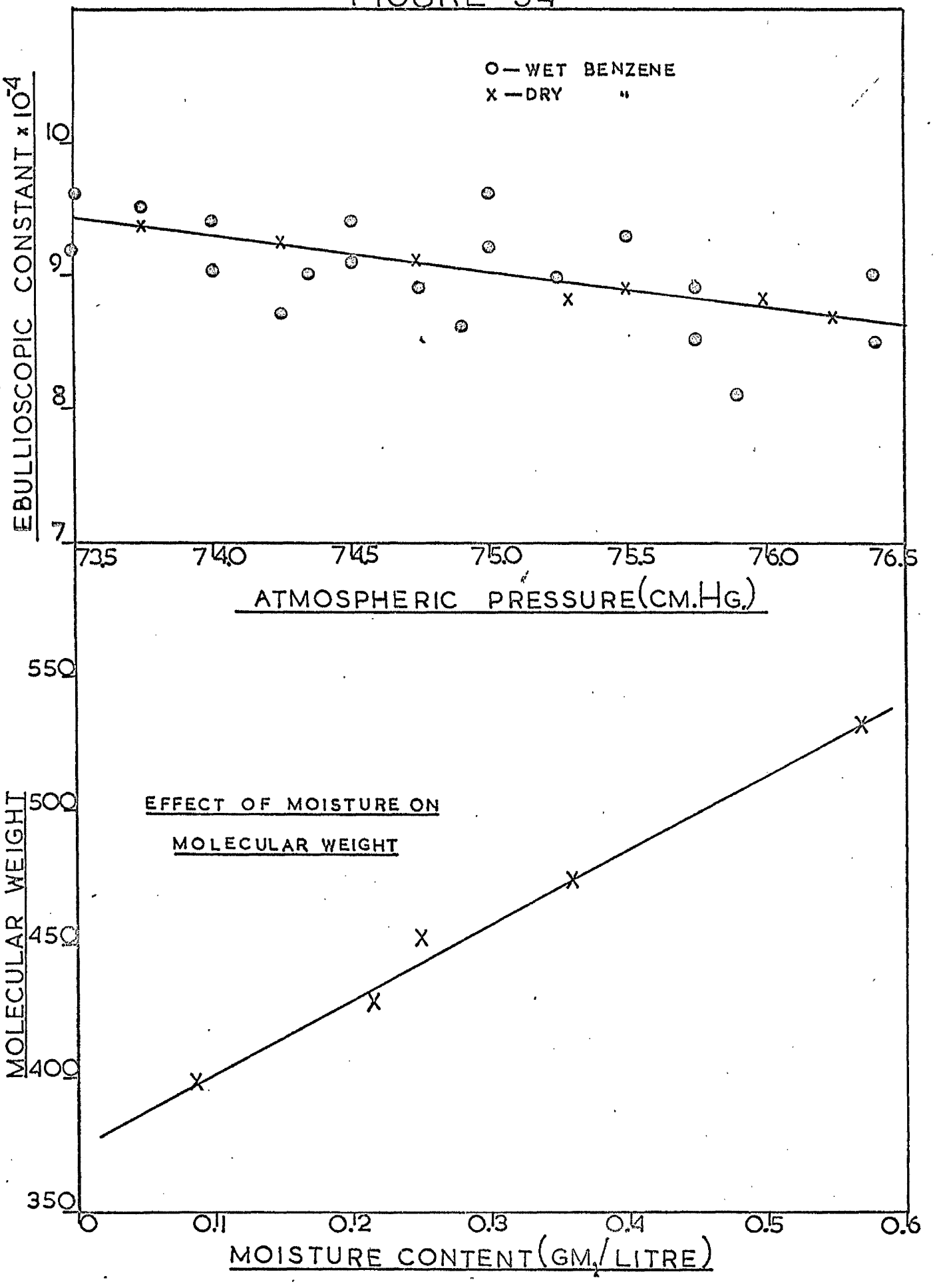

⊙ – BEFORE MODIFICATION
⊙ – AFTER "
K(INFINITE DILUTION) = 104,300
ATMOSPHERIC PRESSURE = 770 MM HG.
K(INFINITE DILUTION) = 85,000
EBULLIOSCOPIC CONSTANT x 10⁻⁴ (K)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
0
0.1
0.2
0.3
WEIGHT OF DIMETHYL NAPHTHALENE (GM.)

FIGURE 54


O — WET BENZENE
X — DRY "
EBULLIOSCOPIC CONSTANT x 10⁻⁴
10
9
8
7
73.5
74.0
74.5
75.0
75.5
76.0
76.5
ATMOSPHERIC PRESSURE (CM. HG.)
EFFECT OF MOISTURE ON
MOLECULAR WEIGHT
MOLECULAR WEIGHT
550
500
450
400
350
0
0.1
0.2
0.3
0.4
0.5
0.6
MOISTURE CONTENT (GM./ LITRE)

The determination of water content was carried out by means of the Karl Fischer method which involves the reaction between iodine, sulphur dioxide and small amounts of water. Equation for the reaction:

$$I_2 + SO_2 + 2H_2O \rightleftharpoons 2HI + H_2SO_4$$

The determination can be done by a potentiometric titration using platinum electrodes, and when a sample is directly titrated with the Karl Fischer reagent a galvanometer inserted in the circuit shows a deflection whenever free iodine first appears - that is a "dead stop end-point".

It was found that the presence of moisture had a considerable effect upon the molecular weights calculated by the method described earlier. The effect is well illustrated by figure 54.

From this it was clear that the presence of moisture in the solvent caused on increase in the calculated molecular weight and hence care must be taken to keep the solvent dry. This was done by re-distilling the solvent and storing over sodium wire and avoiding contact with the atmosphere as much as possible.

The determination of the molecular weight of oils was therefore carried out during this work using benzene which was carefully dried as described above. Using this modified technique greater accuracy was obtained when calculating the ebulliometer constant, which now showed a definite linear relationship with barometric pressure (figure 54).

V. REFRACTIVE INDEX

An Abbe Refractometer, reading to the sodium D-line, was used for this purpose. Measurements were made at 20°C. temperature control being

maintained by pumping water from a thermostatically controlled bath through the refractometer. The accuracy of the instrument was frequently checked with distilled water and 1-bromonaphthalene.

VI. DENSITY

This was measured using a U-tube pycnometer similar to that employed by Van Nes and Van Weston (28) and Lipkin et al (121). The pycnometers described by these workers had open cups at the top of each limb to cope with expansion of the liquid and filling of the pycnometer, but in the present work these were omitted because filling took place at a little under 20°C. and there was very little expansion.

No buoyancy correction factor was applied during calibration or density determination, but an apparent volume was calculated and used to determine the apparent density. The value obtained in this way differs only very slightly (in fourth decimal place) from the actual density and by applying an equation, as did Lipkin et al, the true density in vacuo can be calculated.

The apparent volume of the pycnometer was found by filling it with distilled water, at just below 20°C., by means of a vacuum pump. The filled pycnometer was then placed in a thermostatically controlled bath at 20°C. ± 0.01°C. for approximately 20 minutes, the excess water being carefully soaked up by filter paper from the ground glass tops. On removal from the water bath the pycnometer was dried on outside, washed with acetone, dried again and weighed accurately. Knowing the weight (in air) of distilled water contained in the pycrometer at 20°C. and the density of water at 20°C. (0.99823g/ml.) the apparent volume can be calculated.

Apparent densities of oil samples were determined in a similar fashion and the true density in vacuo being calculated from the following equations:

$$C = 0.0012\ (1-d_A)$$

and $$d_r = C + d_A$$

where C = correction factor,

d_r = true density,

and d_A = apparent density.

VII. VISCOSITY

The kinematic viscosities of the various oil samples were measured according to the procedure laid down by the Institute of Petroleum (I.P. 71) for use of suspended level viscometers. The miniature version of this type of viscometer was employed since very little oil sample was required (approximately 5ml). Temperature control was achieved by means of a thermostatically controlled water bath and calibration of the viscometers carried out according to British Standard Specifications (B.S. 188).

VIII. ACIDITY

Acidity was determined as mg. KOH/g. oil by the procedure described in A.S.T.M. D664 as a standard potentiometric method. A Pye "Dynacap" pH meter was used in the present work to determine the acidity of 3g. samples of oil dissolved in a 50:50 mixture of n-butanol and toluene. This solvent was employed because it was found to be a better solvent for oxidised oils than a 50:50 mixture of iso-propanol and benzene.

IX. CARBON RESIDUE

The carbon residue of any oil sample was determined by means of the I.P. 14/45 test (Ramsbottom). This method determines the amount of carbon residue

left when an oil is evaporated by heating in a glass bulb at 550°C. for 20 minutes. The amount of residue is then expressed as a percentage by weight of the original oil sample.

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A STUDY OF THE OXIDATIVE DETERIORATION OF MINERAL LUBRICATING OILS.

SUMMARY

APRIL, 1966

SUMMARY

The effect of oil composition on its behaviour under oxidative conditions, both by air-blowing and in an internal combustion engine, was the main purpose behind this research programme. Initially it was necessary to devise techniques for the accurate determination of molecular weight and chloroform insolubles, and to modify various other methods of analysis so that they were suitable for this particular work.

An ebullioscopic technique involving the use of a thermistor sensing element was used to determine molecular weight, but rather severe fluctuations were experienced in the meter readings. In an attempt to rectify this the cold finger condenser was replaced by a permanently fixed Liebig condenser - thus giving a constant volume of solvent in the ebulliometer. However, this was not the complete answer to the fluctuations, these being finally eliminated by the use of benzene (as solvent) which had been carefully re-distilled and dried over sodium wire. Apparently moisture was the principal factor causing the inaccuracies.

Segregation of that part of the oil insoluble sludge derived from engine wear and blow-by particles was carried out by taking up the engine deteriorated oil in chloroform and filtering off the extraneous material. This was made possible by the ease with which the oil and the sludge produced by oxidation of the oil could be dissolved in this particular solvent. The minimum amount of chloroform required per gramme of deteriorated oil was established, as was the most efficient method of solvent removal, i.e. rotary film evaporation. This treatment of the used oil sample did not effect the structure or composition of either the oxidised or unoxidised portions.

In this programme several oils of different compositions were oxidised by air-blowing at 200 C (a modified I.P. oxidation test), and by running under

steady conditions in an internal combustion engine for various periods of time. In general, the pattern of deterioration by oxidation was similar in both systems, i.e. the oxidative deterioration followed the path of:

hydrocarbons → resins → oil soluble sludge → oil insoluble sludge

The oils used in this programme all behaved in a similar fashion under these conditions, but differed from one another in the amounts of various oxidation products produced.

The extent to which any one oil followed the path of oxidation outlined above was apparently governed by the percentage of aromatic material contained in the original oil. Some evidence was obtained supporting the theory of "optimum aromaticity" in the range of 6-8% aromatics. This effect was very evident in oils oxidised by air-blowing but was less obvious when the same oils were deteriorated in the engine.

In this work it was shown that a similar optimum effect existed when the ratio of aromatics : naphthenics was considered. At aromatic concentrations lower that 7 or 8% insufficient oxidation inhibiting materials, e.g. naphthols, were formed to prevent the formation of oil soluble sludge, and at this "optimum aromaticity" enough inhibitor was formed to limit the oxidation to the production of resins. Where the aromatic content was high the amount of inhibitor formed was not even sufficient to prevent the oxidation process to proceed yet another step to oil insoluble sludge.

Conditions in the engine appeared to favour oil soluble sludge formation but not the formation of oil insoluble sludge. It may have been that the metals present counteracted the effect the inhibitors formed, thus allowing soluble sludge, and that insufficient time had been spent at engine conditions for insoluble sludge to be produced.

In both methods of deterioration the same hydrocarbon types were oxidised to give similar oxidation products. The material which was removed upon oxidation and treatment with fuller's earth was found to be spread over the hydrocarbon types present in the original oil with a tendency for the heavier aromatic material to be preferentially attacked. This tendency was more apparent in the oils containing most aromatics.

The tendency for hydrocarbons to be oxidised to resins, then to oil soluble sludge, and finally to oil insoluble sludge was made more apparent by the evidence found during this programme of work. A transfer of material apparently took place from resins, via soluble sludge, to insoluble sludge. In addition, it was found that the acidity of the oil insoluble sludge was related to its insolubility in the oil - this may have been due to the formation of hydroxy acids (by the oxidation of oil soluble sludge) which are known to be insoluble in mineral lubricating oils.